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EQUITABLE RATE-MAKING BY PUBLIC SERVICE COMPANIES

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1. Principles Must Be Formulated

The problems of appropriately fixing rates to be charged by so-called public service companies for the service which they render have been given much quiet study in this country for a number of years. The officials of many companies have given them extended study. The Interstate Commerce Commission has been at it, and some state commissions have also been at it. But there has as yet been little advance made in the methods of treating the difficult problems.

The present storm of discussion, precipitated by the results following the policies of a few impetuous promoters who have secured control of some properties and the work of irresponsible or incapable managers in temporary charge of properties held legitimately by honest owners, seems in a fair way to bring about such acute and careful study of the situation that some principles are likely to be formulated for application as a poultice, to draw out what wrong exists and, as far as may be practicable, to heal the difficulties.

That plungers, corruptionists, or adventurers have had to do with the formation of some of the corporations now enjoying special fran-

chises from the public is not a matter for surprise. Nearly all new businesses which promise to grow to great magnitude become the goal of adventurers. It is only after a business has settled into a stable and permanent state, lacking the speculative element, that it becomes generally attractive to men of established business probity, and surely free from the presence or the attacks of speculative adventurers; and the businesses engaged in by most of our public service companies are so new that the price marks still show and the paint is not yet worn. Even the railroads—strong, stable, necessary to the welfare of the country and its civilization as they are—are mere youths. The Rainhill contest, in which George Stephenson publicly proved the preëminence of the steam locomotive over horse flesh or cables for traction, occurred less than eighty years ago, and the railroads of the world are the offspring of that demonstration. The supply of gas for illumination is somewhat older; but the electro-magnetic telegraph as a realized embodiment is only sixty-four years old, and the grandfathers of most of this audience knew naught of such modes of communication. The speaking telephone has extended only through the life of a generation, and it is no more than twenty-five years old as a force in the service of the public. The arc light of the public streets has seen but thirty years of commercial service, and the incandescent electric light has seen even less years in the service of the public. The commercial electric street railway sprang into life less than two decades ago with the success of the Richmond experiment.

In consideration of their tremendous records of development, expansion, and improvement, affording always a great speculative element in their exploitation, it is not to be wondered that projects utilizing these means for serving the public have at times fallen into the hands of speculators or corruptionists. It is useless to waste hard words upon offenders of the past. The duty of good citizenship lies in acknowledging the honesty and squareness which have been manifested in the management of the great proportion of the corporations serving the public, encouraging the right doers, and calmly evolving suitable plans for preventing the recurrence of wrong caused by the intent or the carelessness of those in control of semi-public corporations.

In seeking for such plans, it is obviously necessary to find sound principles upon which to found them. Two bed-rock principles which fit the conditions under which public service corporations do their business are these:

1. The company is granted certain privileges by the public for the purpose of enabling it to furnish readily some type of service to the people, and it should be expected to furnish service fitting the needs of the people; good of its kind, and at prices which are reasonable when judged by the conditions.

The reasons for stating this first of the bed-rock principles in language like the preceding are so obvious and persuasive that I will not delay for the purpose of marshaling them formally before you; and I will turn to make a statement of the second of the two bed-rock principles, in the following words:

2. The company must not be unnecessarily harassed, but must be afforded every reasonable opportunity for economically transacting the business rightfully related to giving the service for which the company was organized; and it must be allowed to make such clear profits over all legitimate costs of its service that it may attract the best and fairest minds to the management, and maintain a position of stable credit with the investing public.

I think the reasons for stating this second principle in this language are also so obvious that the statement will be accepted by most fair-minded and thinking men without argument, but I will stop here to emphasize the significance of certain portions of the statement. In order that the service rendered by a business corporation occupying a special grant from the public may be all that it should be in the details of operation and in its adaptation to the changing needs of the public as public conditions change (perhaps by growing population, greater per capita use of the service, demands that the service be guided into new channels, or those many other causes constantly pressing on the public service corporations), it is of the utmost importance that the operations of the company shall be managed by high-minded, broad-gauge men of foresight and comprehensive grasp of commercial affairs. But such men are ordinarily not attracted to and cannot be retained in the service of companies which are hampered and annoyed in trivial matters, or are put under the pressure of harsh conditions which prevent earning sufficient profits to pay, on the investors' money actually put into the property, returns which the larger merchants and other business men would hold to be reasonable.

Here, however, we begin to get on difficult ground. One of the first difficulties that we meet relates to capital account. To the man who has not been in executive relations with manufacturing or oper-

ating companies, and has not been connected with industrial affairs, it is natural to assume that the capital invested in a public service plant has been all expended for the labor and material composing the physical property which any one can visually inspect and appraise. Such a man is likely to assume, as a matter of course, that every dollar in the par value of capital stock or bonds which is not represented by such labor and material composing the physical property is superfluous, and therefore of the character usually denominated "water." It is a real shock to such a man, however right-minded he may be, to learn that this view is wrong, and that many expenditures which are outside of "labor and material" are legitimately necessary for the production of an operating plant, and are legitimate charges to capital account.

2. The Legitimate Investment in a Public Service Installation is Greater than the Cost of "Labor and Material" in the Plant

The origination of a project, preliminary surveys and construction plans, and supervising the construction, all cost large sums of money in an important project, and this money is wisely expended because well-matured plans based on full information (though of large expense) conduce to greater assurance of the project ultimately rendering good service at reasonable cost. In other words, it is better to make these expenditures out of capital, rather than risk a poorly planned execution of the project; for experience proves that the latter is likely to cause more cost in the end, and consequently require of the public the payment of higher prices for service.

Expenditures must also be made for fire, fidelity, and casualty insurance during the time the construction of the plant is under way, to protect the company from the chance of being wiped out by the disaster of fire or the damage costs due to some unhappy accident. Costly accidents during construction seldom occur in well-managed work, fortunately, but casualty insurance is a wise precaution to take.

Easements for rights of way often cost an electric light or power company considerable sums of money, and the cost of negotiating for such rights, besides the cost of purchasing the rights, properly belongs in capital account.

The cost of organizing the company, the legitimate lawyers' charges due to the work of organizing the project, drawing and scrutinizing

papers, and the like, and the expense due to bringing the working force up to an efficiency by which the public may be adequately served, all fall within the category of expenditures which belong to the capital account.

Working capital (which is often a large cash sum legitimately required for the maintenance of the business of a company like an electric light or gas company, which sells product by meter and receives its payments from customers only after service has been rendered during a month or a quarter) is properly a part of capital account; and also the cost of taxes paid during construction, the cost for interest during the construction period and while the business is being got under way, and the cost of selling securities issued, or any discounts made for bringing about the sale, belong to capital account.

The last item, brokerage or discounts on securities issued, seems to be without serious dispute in the discussions now progressing. Selling securities obviously must cost money. The printing of the certificates, the advertising, and handling the certificates and handling the money, all call for time, attention, and expense. Where insurance against failure to dispose of all of the securities is also provided by underwriting, as a matter of wise provision against unexpected and expensive delays in getting the money as construction proceeds, this item may be considerable. When so stable a corporation as the Pennsylvania Railroad Company finds a market for its bonds only by selling them several per cent. below par, it is no more than reasonable to expect brokerage or discounts amounting to 8 or 10 per cent. of the securities issued in the instance of new and unestablished projects, and oftentimes the discounts must be even larger.

The item of interest during construction is one which is often disputed, but I think only through misapprehension. The merchant or manufacturer who owns his own business may say that he puts money into his business or plant, and gets nothing out of it until the business has been built up to a profitable basis. This is true, but the same merchant or manufacturer confidently expects ultimately to get returns on his investment, when the profits begin to come in, which are very much greater than the ruling rates of commercial interest on money. The merchant receives the reward of his enterprise, his foresight, his skill, his fidelity, and is reimbursed for the risks at the starting of his business enterprise, by this excess of return on his investment above ordinary commercial interest rates.

The well-established public service corporation which is doing its duty, ordinarily should make its charges for service so reasonable that it can pay the investors a return on their invested money which is only enough higher than the ruling rates of interest to make the securities marketable in the face of the precarious, shifting character of a new branch of business which is subject to all of the changes caused by astounding fecundity in discovery and invention. Under these circumstances, the investors are doubtless justified in expecting to receive interest on their money from the moment they pay it in. Where profits are of the speculative character of a mining project, into which money goes with the hope of getting it out many times over, interest for a year or two on the money put in is of relatively small moment; but when the returns are to be governed by normal interest rates, it is proper to expect the interest to start when the investment is made. This being a just and reasonable view, the company ought to provide for interest during the construction of a new project, and as a matter of fact it ordinarily must do so to attract people to invest in its securities, and thus furnish the money to carry out the project.

These items are not all large, but in the aggregate they ordinarily equal a large percentage (generally a number of tens of per cent.), in comparison with the actual cost of labor and material making the physical part of the plant upon which one can directly lay the finger.

Money for all these expenditures must be raised before the completion of the plant. If the expenditures are not charged to the capital account, they must be raised by the creation of a debt to be paid off from operating receipts, which means that early users of the company's products must pay unduly high prices. The fair way is to charge all to the capital account, and let the receipts from service carry the interest on the investment for these items in the same manner as the interest for the investment in brick and mortar, steel and copper is carried. It is therefore unreasonable to criticise a public service company merely because its issued securities have a larger face value than the value of the physical property which may be set down in a schedule, but the situation should be carefully scanned to see whether the difference is beyond legitimate limits before criticism is passed.

The Interstate Commerce Commission enumerates the items pertaining to steam railroads, and belonging in the category to which I am referring, in the following manner in its CLASSIFICATION OF EXPENDITURES FOR ROAD AND EQUIPMENT (that is, the company's investment

upon which interest must be paid), separating them in a somewhat different manner from the way in which I have separated them in the foregoing statements, but including them all as part of the legitimate capital account:

1. ENGINEERING.

To this account should be charged salaries and expenses of all engineers, assistants, and axmen; cost of teams for transportation of engineers and men to and from work, or upon trips of inspection of line of work, or incidental thereto; engineers' instruments, rods, chains, axes, hatchets, tape lines, keel or marking chalk, stakes, profile and drawing paper, tracing linen or paper, cross-section paper, transit and level books, cross-section or topographical books, India ink and colors, drawing boards, stools, map cases, fuel, lights, camp equipage, and other analogous items.

Note.—When employees enumerated above are engaged in work not chargeable to construction, their pay and expenses should be charged to the specific work on which engaged.

2. RIGHT OF WAY AND STATION GROUNDS.

To this account should be charged the . . . salaries and expenses of counsel, right-of-way agent, and engineers and assistants, when specially engaged for such matters; cost of stakes used to denote right-of-way limits; expenses of appraisals, or of juries, commissioners, or arbitrators in condemnation cases; cost of removal of buildings (if upon right of way or station or terminal grounds, and not included in property purchased); commissions paid outside parties for purchase of properties for these purposes; cost of plats, abstracts, notarial fees, recording deeds, etc.; and payments for abutting damages.

Note.—The estimated salable value of property not required in connection with the operation of the road after completion thereof, but acquired and charged to this account in connection with land needed for right of way and station grounds, should, upon completion of the road, be credited to this account and charged to an appropriate property account. Where such property is sold upon or prior to the completion of the road, the proceeds of sale thereof should be credited to this account.

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32. TRANSPORTATION OF MEN AND MATERIAL.

To this account should be charged the fares of laborers and freight charges on material, outfits, and supplies employed in construction work, paid by the railway company and properly chargeable in expenditures for road, but which cannot be correctly charged under any other construction account. This account may include such items as fares of contractors, their walking bosses, paymasters, clerks, and storekeepers; of labor agents; of men hired by labor agencies and shipped out on the line, who may be employed on any character of work; freight on powder, dynamite, and other explosives, hay, grain, groceries, and other supplies for contractors, stores to be sold to sub-contractors, station men, laborers, and others; and other analogous items.

33. Rent of Equipment.

To this account should be charged rent, either on the basis of per diem, mileage, or at fixed rates per month, of all equipment (the cost of which is not charged to the line under construction) used in construction of new lines.

34. Repairs of Equipment.

To this account should be charged repairs and renewals of all equipment used in construction of new lines, not otherwise provided for.

35. Earnings and Operating Expenses during Construction.

To this account should be charged the cost of operating a piece of road while in charge of the construction department and before it is opened for commercial operation. It includes the cost of running construction, material, or other trains when the cost of operating such trains cannot properly be charged to any specific account. To this account should be credited amounts collected for rents of buildings and other properties, and for the transportation of commercial freight or passengers on construction, material, or other trains.

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43. Law Expenses.

To this account should be charged expenditures of the following nature, incurred during the progress of the construction of a road, namely, the pay and expenses of all counsel, solicitors, and attorneys, their clerks and attendants, and expenses of their offices, law books, printing briefs, legal forms, testimony, reports, etc.; fees and retainers for services of attorneys not regular employees of the company; payments to arbitrators for the settlement of disputed questions; costs of suits and payments of special fees, notarial fees, and witness fees; and expenses connected with taking depositions; also all legal and court expenses.

When any of the expenses above enumerated can be charged directly to the account for which incurred, they should be so charged, and not to this account.

(Expenses in connection with condemnation of right of way or station and other grounds should be charged to account Number 2, "Right of Way and Station Grounds," or account Number 3, "Real Estate.")

44. Stationery and Printing.

To this account should be charged cost of stationery, stationery supplies, postage, and printing blank books and forms used by all classes of employees in the prosecution of construction work, not otherwise provided for.

45. Insurance.

To this account should be charged insurance premiums paid on property of the line under construction and before the road is opened for operation.

Note.—Where insured property is damaged or destroyed, the account to which such property was charged should be credited with the amount of insurance recovered in respect thereof.

46. Taxes.

To this account should be charged state, county, township, city, school, road, and all other taxes and assessments levied and paid on property belonging to the company while under construction and before the road is opened for commercial operation, except special taxes assessed for street and other improvements, such as grading, sewering, curbing, guttering, paving, sidewalks, etc., which should be charged to the account to which the property affected was charged.

47. Interest and Commissions.

To this account should be charged cash commissions and the actual cash value of other commissions on securities sold; interest, cash commissions, and the actual cash value of other commissions on loans effected and on notes issued for money borrowed for construction purposes or for purchase of equipment; interest on overdue payments to contractors or other creditors; and interest, cash commissions, and the actual cash value of other commissions and exchange on other commercial paper issued for similar purposes. Interest on bonds and other securities, including equipment bonds or car trust notes, paid or accrued during construction and before line is opened for operation, is chargeable to this account. To this account should be credited all interest received on moneys acquired for purposes of purchase or construction of road or equipment.

48. Other Expenditures.

To this account should be charged organization expenses, including the payment of all necessary fees; the cost of printing certificates of stock and bonds, with payments to trustees and expenses incurred in the disposal of securities; salaries and expenses of executive and general officers of a road under construction; clerks in general offices engaged on construction accounts or work; rent and repair of general offices when rented, with the furniture and office expenses; also all items of a special and incidental nature which cannot properly be charged to any other account in this classification.

3. Effect of Interest on Investment on Public Service Rates

Interest on the investment has a much larger influence on the rates of a public service corporation than ordinary mercantile experience might lead one to believe. Merchants, bankers, and other business men expect to turn over their capital in every year, and it is not unusual in mercantile business to turn it over several times a year. This reduces the proportion with which the interest on investment enters the prices which must be charged to customers, because the interest is spread over sales aggregating from one to many times the amount of the capital. In most manufacturing branches it is likewise common to turn out annual product of value greater than the capital invested. If the value of product made and sold in a year is twice the amount of the invested capital, it is obvious that 10 per cent. profit on the value of the product,

earned above all manufacturing costs and charges, means 20 per cent. profit on capital.

On the other hand, most public service companies are situated under conditions quite the contrary from those pertaining to the projects of general business and manufacturing. Instead of making a gross annual income equal to or exceeding the capital investment, an electric light company ordinarily must expend a sum of money in establishing its plant and business which is not less than three or four times the annual gross income that it may expect to receive, and which must often be from four to six times the gross annual income. This at once multiplies the influence which interest on capital exerts when charges for service are to be determined, which is exactly the contrary of the conditions which pertain in most of the branches of general business and manufacturing. A public service corporation of this character, therefore, cannot do business on the usual margin of general "manufacturing profit" and live; but a larger proportion of its annual gross income must inevitably be available for meeting the demands of interest, or the project will fail.

4. Good Judgment in Management of Highest Importance

The problem of fixing rates for public utilities falls into even greater difficulties when we come to consider the expenditures during operation. As in the question of the capital account, all expenditures that are illegitimate must be suppressed, but all legitimate and reasonable expenditures which go to improve or cheapen the service and advance the stability of the company must be provided for and allowed. The difficulties here are twofold: First, the difficulty of drawing an exact line between expenditures that should be allowed, and expenditures that are not illegitimate but may not be of sufficient permanent usefulness to the company and its service to justify the expense. Second, the difficulty of determining in what manner and how extensively to provide for various perfectly proper future expenditures that will become necessary to prevent impairment of the capital.

Under the first of these categories come expenditures for several purposes, of which I will name only one which is very often criticised unsparingly, sometimes even in instances where a careful scrutiny would show that the disparagement is unmerited. The expenditures to which I now refer are those for advertising (or pertaining to the

publicity, or new business department, as it is nowadays often called). It is a manifest truth that there can be no reasonable disapproval of advertising that results in a betterment of a company's operating condition so that it can better serve the public or afford its customers lower rates; but determining where this condition ends and a waste of money begins is largely a matter of judgment, and may not be conservatively done.

The ambition to increase the business is one to be encouraged when accompanied by good judgment, and the advertising required to bring about an advantageous increase makes a cost which is undeniably to be encouraged. There are instances, however, in which "publicity" has seemed to become an obsession, and then the cost of advertising has become excessive and has not rendered adequate returns. Obviously, increased business is without advantage for itself alone, so far as the interests of the public are involved, and only that kind of increase should ordinarily be encouraged which brings more satisfactory operating conditions, and therefore improves the service or reduces the cost per unit of service or of product. Advertising which brings returns of that kind, thus paying its own cost and in the end affording advantage to the public, is to be encouraged, however great may be the expenditure; but the kind of publicity which costs more than it brings back to the service, or accomplishes only such temporary results that it makes no profit over its own cost, seems to me to verge on the illegitimate.

Every item in the annual expenses of a public service company which falls in the category to which I am referring should be treated in the manner just applied to advertising. But the difficulty of drawing the line clearly between the right and advantageous and the disadvantageous is almost insuperable. After observing the really marvelous returns which have been obtained from extraordinarily large expenditures for advertising made by certain gas companies and electric light companies, I do not see who is to say in advance, in any particular case, where such expenditures exceed propriety, so long as they are made in a legitimate way. Good judgment combined with caution seem to afford the only guides, and this equally applies to all branches of the operation of a company. Good judgment, then, looms large as an element of the utmost importance in the management of public service companies, if the public is to enjoy low rates and good service; and, honesty and good judgment being established in the saddle, they probably can bring the best results for the public if afforded a large degree of independ-

ence within limits wisely placed by honest legislative bodies. In order that honesty and good judgment may be first established, and then maintained, in the saddle, the full recognition by legislative bodies and commissions of the second principle which I have previously urged is of great importance. Competent men with a combination of the needful fertility, enterprise, integrity, and fidelity cannot be attracted to and permanently attached to projects unless wide scope is afforded for their individual abilities and adequate compensation is made for their services. The possibilities before an able man in general business make it impossible to circumscribe the legitimate opportunities in a public service company and at the same time attract able men to officer the company.

5. Depreciation and Its Allied "Deferred" Accounts

Difficulties of the second order above named, *i. e.*, those relating to provisions for expenditures which will become necessary in the future to prevent impairment of capital, mostly relate to conditions which impose reasons for gradually accumulating a reserve fund from which extraordinary demands for expenditures may be met. Depreciation of plant and the kindred accounts which may be known as "obsolescence" and "required reconstruction" are embraced within these conditions.

A great deal of confusion exists in regard to reserve funds of the kind to which I refer. A public service company which sets aside reserve funds adequate to prevent future impairment of its capital through the depreciation or obsolescence of its plant is often subject to violent attacks by people who are not acquainted with the character of the industries involved. This has led in some instances to a surreptitious treatment of such accounts, which produces a constant temptation to corruption.

There is also confusion in the minds of the people who are in the management of public service companies in respect to the scope of these accounts, and this has sometimes caused abuses in regard to capital charges, sometimes entirely unintentionally.

The technical meaning of depreciation is perfectly well defined. It is well known that any mechanical plant, however well cared for and kept up by current repairs, gradually deteriorates so that it must ultimately be replaced. For instance, a locomotive, kept in the fittest

condition practicable throughout its life, ultimately comes to a point where its general decrepitude puts it beyond the help of rebuilding and repairs, and renders its further use unsafe. It must then be replaced bodily. This gradual deterioration, which constantly goes on and ultimately terminates the useful life of most structures, constitutes depreciation. In the case of a long-established railway system, owning thousands of miles of track, hundreds of locomotives, and tens of thousands of cars, the depreciation may be cared for year by year by each year retiring a suitable number of locomotives and cars and replacing them with new, and rebuilding a suitable proportion of track and other structures each year. In this way the depreciation may be cared for by the expenditure of approximately equal sums of money each year, and the account can be merged with the account for those repairs which are of the current character called "current repairs," and illustrated by the work of the section gangs and the periodical overhauling of locomotives to keep them in economical working condition throughout their useful life.

Few of the other public service companies have reached a magnitude or their art a permanency which enables them to carry the brunt of depreciation in this manner. A telephone company may find it necessary to rebuild an entire line of poles once in ten years, and an electric light company may find it necessary to replace a battery of boilers or an engine-generator set at the end of twenty-five years of useful life. Owning relatively few such units, these companies must treat the expense of such replacements as an extraordinary account, differing from current repairs which can be provided for month by month and year by year at a fairly uniform rate depending upon the business. It is obvious that a company may not be able to meet the extraordinary expense referred to from the income of the particular year in which the replacement becomes necessary, and it is manifestly proper for the company to anticipate and prepare for the situation by accumulating and maintaining a reserve fund which will be sufficient to meet the replacement expenditures as they become necessary. This is the object of the depreciation reserve, or "reserve for reconstruction," as it is called by some, which is commonly maintained by electric light, electric railway, and telephone companies. Its object is manifestly proper, and maintaining such a fund rests on the foundation of honest business judgment.

Two other factors are associated with depreciation in such a manner that they also must be provided for, by most public service companies,

by the accumulation of a reserve fund to meet the extraordinary expenditures which they put upon the company at intervals. These factors relate to the development of the art, which may make an expensive plant obsolete before its natural life is run, and to the reconstruction requirements laid upon the system from time to time by legislation. The first of the factors is commonly referred to as "obsolescence," and it is a factor of much moment in those branches of the business in which the art is changing rapidly on account of fecundity of invention. If a telephone company installs and puts in operation an expensive switchboard and equipment of the most approved type of the day of its installation, but invention shortly thereafter produces apparatus by means of which much more convenient service may be afforded the telephone users, the company is soon forced by the clamor of its customers to substitute the new type of plant for that in use. This is an illustration of obsolescence. The plant in use might have years of natural life before it according to ordinary considerations, but the advance of the art rendered it obsolete; whereupon its replacement was necessary to maintain the business at a satisfactory state. The expense of this replacement might amount to a large part of the company's annual income, or perhaps more than the entire income for one year. It would be unfair to charge the expense of such replacements to the account of capital (bringing in new money for the purpose), as the company has no greater property after the replacement than before, and such a procedure would effectually preclude the possibility of any future reductions of rates to customers or improvements of service; but the proper way to meet the expense of such replacements is to provide a reserve fund, accumulated by annual additions after the manner of the depreciation reserve, and maintained for use when required.

The second of the two factors to which I am now referring differs from obsolescence in form, but possesses like characteristics in operation. I have called it "required reconstruction," for want of a generally adopted term. An electric light company may own a well-built pole line, in excellent condition, which borders a street upon which the city authorities order boulevard improvements, and the wires must go underground. The overhead line had been originally constructed according to good business foresight, as the improvement of this street was not then contemplated; but the required reconstruction involves a large loss on the pole line, because the salvage of material upon its removal is by no means equal to the cost of the construction of the line. A farsighted con-

sideration of the interests of the stockholders of the company, and of the public who are the company's customers, seems to me to call for making good this loss out of a reserve accumulation built up and maintained after the manner of the depreciation reserve. The cost of the new underground construction which replaces the pole line seems to be a proper capital charge, because the company possesses permanent property in that construction and the people living along the improved streets and buying the electric current from the cables may be expected to pay interest on that property. On the other hand, if the old pole line (now removed) is left in capital account, a load is put on future service which may preclude the further and constant improvements in character of service and plant which the public desire, and it seems to the advantage of the public to have the loss which is imposed on the company by the required removal of the pole line made good out of a previously accumulated reserve. The increase in the company's investment on which interest must be secured from the customers, which is caused by the transaction carried out in the manner indicated, is equal to the amount by which the cost of the new underground construction exceeds the then value of the removed pole line, and the sum which must be provided from the reserve fund in carrying out the transaction is equal to the first cost of the pole line diminished by the salvage.

These three factors of depreciation, obsolescence, and required reconstruction may therefore be treated as a unit in the bookkeeping of the company, and a single reserve fund may be accumulated and maintained for their support. As an engineering matter they are separate, but this does not prevent a suitable treatment of them as a unit in the bookkeeping. The commission appointed by the city of Chicago, some two years ago, to study the telephone system in that city, made a careful study of the sum of money which ought to be set aside each year so that the accumulated funds might adequately meet the requirements of these factors as they arise. The report of the commission points out that the annual addition to the accumulated reserve fund ought to average 8 per cent. of the first cost of the plant, including the company's buildings, but not including its land. This 8 per cent. is also separated by the commission into two parts: one, 5¾ per cent., to account for depreciation and obsolescence; and the other, 2¼ per cent., to account for estimated required reconstruction and a small proportion of fire insurance risk which, in this instance, cannot be economically placed with insurance companies. The apparatus of telephone companies is delicate and

fragile, and the telephone art is in a period which is fertile with invention and improvements, which make the rate of depreciation and obsolescence quite large in telephone plants. These factors for electric light, electric railway, and gas light companies are ordinarily counted at a lower rate than the 5¾ per cent. computed by the Chicago Commission for telephone investments in that city.

Some add to these factors an additional one, which they call "inadequacy," which is intended to include a somewhat indefinite expense that may be caused by building a plant piecemeal as the business progresses and develops, instead of all at one time. This manner of building often results in the property units proving too small for the most economical service after the business has gained development, and expense must be incurred for rectifying the error which was essentially due to lack of courageous foresight and understanding of conditions which the future only could expose. It seems to others more reasonable to class expense of this kind as a part of the capital required to develop the business, rather than a factor which may be forecast with some degree of accuracy and cared for out of an accumulated reserve. I will, therefore, here dismiss it without more detailed consideration of its character.

6. The Test of the Equitableness of Rates

My object in dwelling at some length on these details is to bring forcibly to your mind the fact that the normal expenses of operation (including taxes) and the interest on invested money are not the only items involved in a consideration of what constitute equitable rates to be charged for its product or service by a public service corporation, but that reserve funds for reconstruction requirements (and sinking funds needed when the company operates under a fixed term franchise) must be given due consideration. This fact is very often neglected or forgotten in the course of criticism leveled against public service companies. Frank and reasonable criticism will never injure any right-minded corporation, but unjust criticism seldom comes to good. It is natural for the uninitiated to cry out for a large reduction in rates when he learns that the normal expenses of operation of a public service company, such as an electric light company, consume in a particular year (we will say) only 60 per cent. of the total receipts from the customers. An average reduction of the rates by 25 per cent. may appear to him to still leave a goodly margin for the stockholders, but his deductions

are without substance because they are made in neglect of certain important factors which analysis will disclose. I will choose a particular company, for illustration, which has an annual gross income in a certain year equal to substantially one-third of the investment in the property (which is a favorable figure), and for which the average yearly sums set aside for the reserve for depreciation, obsolescence, and required reconstruction ought, according to careful engineering judgment, to amount to not less than 6 per cent. of the invested capital of the company. In this case 18 per cent. of the annual income should go to the reserve to be expended in renewals and reconstruction, or the service will ultimately depreciate and the interests of the customers will suffer in spite of any wishes of the company to the contrary. Sixty per cent. of the annual income is consumed in normal or current expenses of operating (including taxes), and the returns on the capital invested may be made out of the 22 per cent. of the income which remains as a balance. Even if all of this balance is paid to the investors, it does not give to them 22 per cent. on their investment, but only 7⅓ per cent., since the gross annual income is only one-third as great as the invested capital. Seven and one-third per cent. is a large return to expect from mortgage bonds of a great corporation like a railway company, owning some thousands of miles of track and carrying on a profitable business in a diversified territory; but it is small as a return on capital risked in general business or manufacturing, and the average business of the electric light companies, electric railway companies, and the like, partakes of risks resembling those of general business concerns. The obvious deduction is that any reduction in the rates under consideration may be very unwise, because it may cripple the credit of the company, and thereby prevent it from obtaining money to continue a policy of extending its plant and widening the usefulness of its service. Such crippling of a well-managed public service company is likely to curtail the advantages which it can afford its customers (with whom the city itself is generally included, in addition to the large numbers of individual citizens), producing widespread inconvenience to a degree that far more than neutralizes any saving which the customers can make as the result of a small reduction in rates. In the particular instance which I have used for illustration, a reduction of the rates by an average of only 4 per cent. would reduce the margin left for the return on the investment to 6 per cent. of the invested capital, in case the other charges were duly provided for by the company out of its income. This is too narrow a margin

on which to establish the success of an electric light or telephone company, for instance, except in the cases of the largest and most firmly established concerns which enjoy unlimited franchises.

The two bed-rock principles which I named in the early part of this paper seem to me to be equally applicable to the conditions existing in parts of the country which are new and yet to be developed, and in stable and well-settled parts of the country; and the same seems to me to be true of the considerations which I have discussed in association with the two principles. But the deductions cannot be drawn to apply unqualifiedly to all parts of the country. In new parts of the country, the need of the service and the advantages coming as a result of the service may be far in advance of the capital readily available for building plant to render service, and the risks of embarking in projects in an undeveloped region deter investors from furnishing capital unless every reasonable opportunity is opened by the governing authorities for the service company to earn extraordinary returns on the invested capital. The investor who is satisfied with 5 per cent. return per year from an investment of proved permanency may with reason consider 10 per cent. too small to overcome the risks which are united with the earlier years of a public service investment in a new but "hustling" Western city which grants a franchise for a limited term of years. These risks involve many factors which are not found in general business, for a fixed investment in permanent plant must be made from which little salvage can be recovered in case of failure, and success may be accomplished only through shrewd forecasting the character and rapidity with which the city will develop and appraising the stability and personality of its citizens. A manufacturer may ship his product elsewhere, a merchant may move elsewhere with small loss, but a local utility company is rooted to the ground, and the risks surrounding its existence when established in a new though hopefully developing country are correspondingly large. Such a company is also and additionally subject to the chances of ruinous competition, which may be brought on by speculators invading its field in a territory not yet rich enough to support adequately one company, and to the attacks of political and other "strikers" who wish for favors.

This leads me to a third and a fourth basic principle concerning the matter under discussion, which I will state in the following language:

3. A public service company in a new and developing country must see before it opportunity to earn returns on its invested capital which are very large compared with those adequate in stable and thickly settled

regions, in order that it may secure the capital needful for developing its plant and extending its service to meet the apparent needs of an expanding but not yet stable population. If opportunities for honestly earning large returns on the investment in a new country are curtailed by legislation, the development of the service must become inevitably retarded to the disadvantage of the country.

4. A new company, even in a stable country, ought to earn more than current rates of interest for its investors whose enterprise enables them to take the risks of establishing the business, but the rate of return on the investment may be expected finally to approach current rates of interest after the business has become profitable and is firmly established on fixed franchise rights covering a long period.

The fourth principle points to the corollary that the public service companies, well established in the old and permanently settled portions of the country, which have elected to do business under franchises without term limits and are guarded from unjust competition, which conditions now exist in several of our states, must finally expect to give their best grade of service at rates which earn a margin for the investors which is little or no greater than the rate of current interest for tried and sound commercial investments.

The marvelous growth which has hitherto characterized the business of the public service corporations has confined the attention of the officers almost exclusively to the problems connected with the operations of providing service, and has prevented them from giving close attention to the questions involving the relative equitableness of the rates charged for service. In many instances, the condition has resulted in every effort being bent toward the direction of improving and extending equipment and methods of operation, allowing the questions of rates for service to rest entirely on traffic demands and individual judgment applied to specific cases. The books of a large proportion of public corporations do not marshal their data in such a way that the cost of performing service under different conditions can be determined, and the only means for arriving at a basis of rates, then, is that of business expediency or the individual experience of the officials. I think that it may be truthfully said that the latter, applied in a balanced manner, normally tends toward the production of equitable rates, but business expediency applied to individual cases as they arise is likely to lead the other way. However, neither of these methods of fixing rates can be considered either as reasonable or as giving assurance of relative equity in the treatment of customers.

The question of "what the traffic will bear" must always be an element in the determination of rates for public service corporations. This phrase, "what the traffic will bear," has a real significance of great merit, which differs from its popularly accepted meaning of taking all that the customers will give up. According to its correct meaning, it signifies that the charges made for service are adjusted as between the company and each of its customers, so that the company finds the dealings profitable with each, when the full situation is considered, and each customer receives service which as nearly as practicable meets his requirements and costs a price which makes the service advantageous to him, while no unjust discriminations between customers are allowed.

In passing, I will make a note that the last phrase does not involve equal prices to all customers, but does involve the treatment of all customers so that they obtain from the company relatively a full return for their money. An illustration of this statement may be found in considering rates that seem equitable to charge for electric lighting.

In substantially every extended electric lighting project there are a number of consumers who use their electric light for very short periods, occurring only during the hours when the electric lighting plant is carrying its heaviest daily load. The inherent characteristics of the electric lighting business, as we know it, make it impracticable to store commercially large charges of electrical energy, and it is therefore found that loading a plant with this class of service alone makes the cost of the service substantially prohibitive, as all of the interest and depreciation upon the large installation required must be earned from output delivered in short periods each day. The customer who uses current only from five o'clock to six o'clock every week day may cost the company seventy-five dollars per year for fixed charges for every kilowatt in his maximum use (or "maximum demand"), and a rate of twenty-five cents per kilowatt-hour might not be an unreasonable charge to make for his service; while the customer who occupies a dark basement and uses his lights for eight hours per day may cost the company no greater aggregate for fixed charges. Though the latter customer imposes on the company a larger expense for fuel and other operating expenses, the total cost of service to him is relatively smaller, and a price of five or six cents per kilowatt-hour might not be unreasonable to make. If means for storing electrical energy were available of the same convenient cheapness as gas holders for storing gas, the differences would not occur so startlingly. They are more startling in the electric light service than in

the business of most of the other purveyors of public utilities, and the electric light companies have therefore come into the habit of making a sliding scale or "maximum demand" charge for service. The electric railway crowds its passengers into standing room in the cars at the rush periods of the day, and then gives poorer service for the same price as the better service of the normal hours, thus reaching the analogy of a penalty charge for service demanded in the rush hours. This is a condition found in many branches of business. The manufacturer of seasonable goods holds prices stiffly while the demand is large, and makes concessions to close out his stock as the season approaches an end. Retailers do the same. The purchase of a straw hat calls for the payment of a price at the opening of the season which may be one-half larger than the price which will command the same hat two months later. I will not multiply the illustrations. The "maximum demand" charges for electric lighting are based on the existing peculiar conditions of electric lighting and the common experience in commercial affairs, so that the employment of such charges cannot be dismissed as inequitable in spirit, though they result in different rates being paid by different consumers per unit of electrical energy consumed.

The test of equitable charges depends, first, upon their bringing in a total income sufficiently large to pay on the invested capital a return which is reasonable under the conditions of the location, after all normal current expenditures relating to operation are paid and adequately adjusted reserves are provided for. What a reasonable return on the invested capital may be is not a matter that can be fixed once for all or for all locations by dogmatic methods, but it is a matter which must be determined by a consideration of custom and the application of common sense to each instance or class of instances, in a manner analogous to the process by which the common law has developed.

The test of equitable charges depends, second, upon a fair distribution of the charges amongst the various customers, and here again fixed guides are lacking and the dictates of custom and common sense must intervene.

In consideration of the facts to which I have referred, it is plain that the test of equitable charges as between customers does not necessarily reside in all customers of a public service company paying at the same rate per unit for their service, or in the price for a given service being constant at all times. It has also been generally accepted that it does not reside in all customers so paying for their service that each

pays cost plus a fixed percentage for profit. It has been more or less generally accepted that the smaller, short-hour users of electric light should be provided with service at a rate which is within their means, even though the rate may not bear its full proportion of the interest on the investment. It has also been generally accepted that some commodities may with propriety be carried by the railroads at rates which considered alone do not bear their part of the cost of operation plus their full proportion of the interest on investment. But if the touchstone of equitable charges is not found in either of these conditions, where can it be found? This is a question to which the answer is now being diligently sought by public commissions and officers of public service corporations. My own tentative answer to the question is: That the test of the reasonableness or equitableness of the rates maintained by a public service corporation is found in: (1) The effectiveness and simplicity with which the schedule classifies the customers, so that the total required income is collected in a manner which secures the same rate for all customers of a class obtaining approximately like service, though customers belonging in different classes, because they obtain service with differences of character which essentially affect the cost per unit, may be subject to quite different rates; and (2) the certainty with which the rates secure from each class of customers the full annual operating cost of the service in that class and such a proportion of the reasonable return on the investment as the customers' traffic can afford. It then becomes a matter of expediency and public policy to determine whether a company receiving a public grant is justified in taking a larger proportion of profit from one class of customers than from another. This policy has been tacitly approved in the case of steam railroads, which are generally thought to do the entire nation a service by cautiously extending lines into undeveloped territory for the purpose of bringing about its development, though the interest on the investment for the purpose, and even part of the current operating expense, may at first be derived from the income secured by the main stem in older and already developed territory. The policy has also been accepted in a limited degree in electric lighting by the more or less general approval of rates for service to short-hour residence users which in many instances do not bring as large a proportion of profit as the rates applied to some of the longer-hour users, though the latter may pay less for each unit of product or service. The question is a relatively new one, and the ultimate limitations of the policy must rest with experience and the future expressed judgment of our most

judicial minds. It would be a manifest injury to the nation if the policy became so circumscribed that the railroads would feel that equal proportions of profit must be earned on all parts of their systems and from all kinds of traffic. What its effect would be in the case of a corporation giving service within the limits of a single city or a single state is not so clear.

Finally, to apply my criterion of the equitableness of rates requires a more effective organization of their cost keeping than has yet come into vogue with most public service corporations. A few of the companies have adopted their schedule of rates as the result of certain actuarial operations, but most of them have arrived at their schedules by the path of gradual modification through experience; and few can support the reasonableness of their schedules on a foundation of facts produced from their accounting records. I believe that this condition is in a fair way to be overcome. Acute attention is now being given by prominent public service companies of all kinds to studying the cost of service, and the making of improvements in records and in methods of analysis are considered with deep interest. I believe that this is a fortunate state of affairs which will result in the gradual removal of many existing ambiguities in the public service rate question, and will also have an effect in allaying the public suspicion and incredulity which now follow many entirely proper acts of public service corporations.

CONTRIBUTIONS FROM THE
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HYDRATES IN SOLUTION: A REVIEW OF RECENT EXPERIMENTAL AND THEORETICAL CONTRIBUTIONS[1]

BY EDWARD W. WASHBURN

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GENERAL PLAN OF THIS REVIEW

DURING the past decade the existence and composition of compounds between solvent and solute in solution has attracted the attention of numerous investigators and resulted in the appearance of a large number of contributions to the problem in recent literature. Since the publication of the monograph of E. Bauer[2] in 1903, however, no systematic treatment of the question has been made.

In view of the widespread interest displayed in this problem, due, no doubt, largely to its important bearing upon the question of solution in general and upon the electrolytic dissociation theory in particular, it has seemed desirable to undertake the collection and systematization of all the recent data bearing upon the question, with the purpose of subjecting the material to a critical treatment. In order to present clearly the principles at the basis of the various methods which have been used in attacking this problem and to evaluate and compare the results with one another, it has been found necessary in many cases (especially in Section I) largely to disregard the conclusions and method of treatment of the individual investigator and to treat his results according to a general plan. Only by some such general system as this is it possible to show the relation of the different methods to one another and to emphasize the relative importance of the results obtained

[1] This review was prepared at the request of the editor of the Jahrbuch d. Rad. u. Elekt., and is published in Heft 4 (1908) of that journal.

[2] Bauer, Ahrens Sammlung, **8**, 466 (1903).

by them. It is believed that this mode of treatment will prove of more value than would a simple collection of the results and conclusions of the different investigators. The necessity for some such procedure as this will be appreciated by any one who has occasion to examine the conflicting conclusions of various authors.[3,4,5]

The methods which have been applied to the solution of this problem and the numerous phenomena for which hydration has been offered as the explanation are so varied in character that their division into classes must necessarily be more or less arbitrary. In the following treatment it will be convenient, however, to treat them under three general groupings.

Section I will comprise all methods which depend upon deviations from the laws of the "perfect solution."

Section II will contain the methods which depend upon kinetic conceptions or upon mechanical interpretations of certain phenomena occurring in the solution.

Under Section III will be classed various methods which cannot be classed with the preceding groups.

SECTION I. METHODS DEPENDING UPON VARIATIONS FROM THE LAWS OF THE "PERFECT SOLUTION"

Introduction

In this group we have the methods which depend upon (1) so-called abnormalities in the effect caused by the solute upon:

(*a*) The lowering of the freezing point of the solvent;
(*b*) The increase in the boiling point of the solvent;
(*c*) The lowering of the vapor pressure of the solvent;
(*d*) The lowering of the solvent power of the solvent;

(2) so-called anomalies in the distribution of a solute between the solvent and a second phase which may be either liquid, gaseous, or

[3] Compare, for example, some of the conclusions reached by the following investigators: Vaillant, Compt. rend., **141**, 659 (1905); Muller and Fuchs, *ibid.*, **140**, 1641 (1905);

[4] Magie, Phys. Rev., **25**, 172 (1907);

[5] Vaillant, Compt. rend., **138**, 1212 (1904); also Bowsfield, R. 90, p. 137, and R. 110, p. 257; and Getman, J. Chim. Phys., **5**, 344 (1907).

solid; and (3) variations of the physical properties of solutions from the law of mixtures.

The methods under subdivision (1) of this group are all identical in that they depend upon the measurement of the same quantity in each case, namely, the active mass, or, as I shall here call it, the "activity" (ξ) of the solvent.[6] They are distinguished from one another chiefly by the degree of accuracy attainable in the experimental measurements, by the range of temperature over which they are applicable, and by the ease or difficulty of their thermodynamic treatment. The results obtained by them can, however, in no sense be regarded as independent pieces of evidence supporting the hypothesis of the existence of hydrates in solution, as has sometimes been done. Being simply different methods of measuring the same quantity (the change in the activity of the solvent) they must necessarily lead to the same conclusions as regards hydration.

It will therefore be necessary to consider only one of the methods in detail. The simplest one, and also the best one from almost every standpoint, is the method depending upon the lowering of the vapor pressure. Owing, however, to the historical prominence of the freezing-point method, and because it is the only one which has received any considerable attention at the hands of investigators, it has seemed advisable to consider it in detail, as this is perhaps the best way to illustrate its inferiority, from a theoretical standpoint, when compared with the method depending upon the lowering of the vapor pressure. The researches of Biltz, and especially of H. C. Jones and his co-workers, have yielded a large amount of experimental material of considerable value.

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[6] I use the term "activity" in preference to active mass, which is a misnomer, since it is not the mass but the concentration which is the determining factor in chemical equilibria. The term "activity" has been recently proposed by G. N. Lewis [Proc. Amer. Acad., 43, 259 (1907); Z. physik. Chem., 61, 129 (1907)]. It has the same qualitative significance which we are accustomed to attach to the less exact expression "active mass," and in most cases it will be necessary to make use of it in a qualitative sense only, but for some instances where the quantity, ξ, will be used in mathematical equations it is necessary to define it somewhat more exactly. This has been done by Lewis (*loc. cit.*). For the present purpose it will be sufficient to regard the activity, ξ, as a quantity which has the dimensions of concentration; for a perfect gas or ideal solution it is respectively equal to or proportional to the concentration, and for other cases may be regarded as a *corrected concentration*.

An equally exact and general treatment could be given by the use of the thermodynamic potential. This quantity, which has been so fruitful of results in the hands of van der Waals, Planck, van Laar, and others, is, however, unfortunately not yet in general use among chemists, and it has therefore seemed best to use here the more familiar, if less fundamental, conception of "active mass."

The Freezing-Point Method

The assumption of the existence of hydrates in aqueous solution as an explanation of certain anomalies in the freezing-point lowering has been a favorite one with investigators of this phenomenon. Fr. Rüdorff,[7] in 1862, assumed the existence of definite complexes between solute and solvent and attempted to calculate their composition. As the result of his investigation of the freezing-point lowerings produced by a number of salts in aqueous solution, de Coppet[8] found that in many instances the ratio of the freezing-point lowering (C) to the mass of salt (M) in 100 grams of water increased regularly with the concentration. He ascribed[9] this phenomenon to the formation of hydrates and calculated the composition of many of them.

Jones and Chambers,[10] in 1900, continuing some previous work of Jones and Knight,[11] determined the freezing-point lowerings produced by a number of chlorides and bromides, and found that the molecular lowering at first decreased with the concentration, reached a minimum, and then exhibited the regular and continuous increase previously observed by de Coppet. The investigation was later extended to a large number of compounds by Chambers and Frazer,[12] by Jones and Getman,[13] and by Jones and Bassett.[14] The investigation of Biltz,[15] in 1902, along similar lines yielded valuable material. The interpretation placed by these investigators upon their experimental data will be understood from the following considerations.

The equation for freezing-point lowering, Δt, in dilute solution may be written,

$$\frac{\Delta t}{n'} = \frac{k(1 + \gamma)}{n}, \qquad (1)$$

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[7] Rüdorff, Pogg. Ann., **116**, 68 (1862).

[8] de Coppet, Ann. Chim. Phys. [4], **26**, 109 (1872).

[9] R. 8, p. 109. "Si les rapports $\frac{C}{M}$ sont *croissant* avec M cela tient à ce que le sel dans les dissolutions a formé au moins une combinaison aux dépens du dissolvant."

[10] Jones and Chambers, Amer. Chem. J., **23**, 89 (1900).

[11] Jones and Knight, Amer. Chem. J., **22**, 110 (1899).

[12] Chambers and Frazer, Amer. Chem. J., **23**, 512 (1900).

[13] Jones and Getman, Z. physik. Chem., **46**, 244 (1903).

[14] Jones and Bassett, Amer. Chem. J., **33**, 534; **34**, 291 (1905).

[15] Biltz, Z. physik. Chem., **40**, 185 (1902).

where γ is the degree of ionization and n' the number of mols of solute dissolved in n mols of solvent. If values of the "molecular lowering," $\frac{\Delta t}{n'}$, determined experimentally, be plotted as ordinates against the corresponding values of n' as abscissæ, the curves obtained for electrolytes show distinct minima in most cases. Examples of this are shown in Figure 1, which is taken from the paper of Jones and Bassett (R. 14, p. 536).

The minimum values of $\frac{\Delta t}{n'}$ occur in solutions of moderate concentration, usually between 0.1 and 0.5 molal. In dilute solutions the increase in $\frac{\Delta t}{n'}$ is evidently due to the increase in γ. If the equation is still valid for the more concentrated solutions, the increase in $\frac{\Delta t}{n'}$ can only be due, since γ is decreasing, to a simultaneous decrease in n, which would result if the solute were hydrated and some of the solvent molecules thus removed from their rôle as solvent. A minimum would, therefore, be produced where these two effects neutralize each other, and the distance of this minimum from the axis of the abscissæ would vary inversely with the degree of hydration of the solute for substances of the same ionic type. The magnitude of this depression has been found to be a function of the nature of the ion, so that if the ions are arranged in the order of their effects upon this depression we should obtain the order of their hydration. Beginning with the ion which produces the least effect, the results of Biltz and of Jones and Getman give the following series:

Chlorides, Cs, Rb, K, NH_4, Na, Li.
Chlorides, Ba, Sr, Ca, Zn, Mn, Cu, Ni, Co, Mg, Fe.
Potassium Salts, NO_3, I, Fl, Br, Cl, CN, SCN.

The earlier experiments of Jones and his co-workers led them to the conclusion that hydrates exist only in concentrated solution, breaking down on dilution.[16] It was, however, pointed out by Biltz[17] that Nernst had shown such a conclusion to be directly contrary to the Mass-Action Law and consequently untenable. In his later work Jones has modified

[16] See Chambers and Frazer (R. 12, p. 519), also Jones and Getman, Amer. Chem. J., 31, 355 (1904).

[17] Biltz, Ber. d. chem. Ges., 37, 3036 (1904).

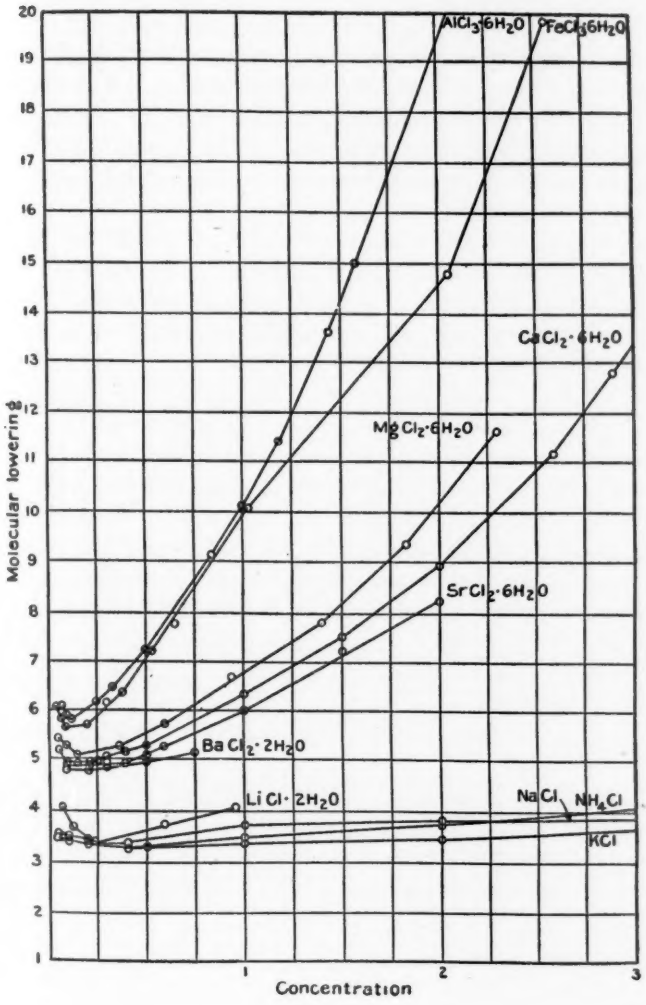
$AlCl_3 \cdot 6H_2O$
$FeCl_3 \cdot 6H_2O$
$CaCl_2 \cdot 6H_2O$
$MgCl_2 \cdot 6H_2O$
$SrCl_2 \cdot 6H_2O$
$BaCl_2 \cdot 2H_2O$
$LiCl \cdot 2H_2O$
NaCl
NH_4Cl
KCl
Molecular lowering
Concentration
1
2
3
4
5
6
7
8
9
10
11
12
13
14
15
16
17
18
19
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FIG. 1

his conclusions so that in most cases they now conform to the Mass-Action Law.[18]

We shall now proceed to examine critically the fundamental assumptions upon which the freezing-point method rests, with particular reference to its availability for the purpose of calculating the approximate composition of the hydrates which exist in solution, a purpose to which it has been extensively applied by H. C. Jones and his co-workers. All such calculations have been based upon the law of Raoult for the lowering of the freezing point, deviations from this law being ascribed to hydration even in the most concentrated solutions.

The law of Raoult for the lowering of the freezing point, like the law of van't Hoff for osmotic pressure, is known to hold, even approximately, only at low concentrations. For an infinitely dilute solution, the former law can be derived rigorously from the latter by means of thermodynamics in the well-known form,

$$\Delta t = \frac{R T_o^2 n'}{\Delta H_o n}, \qquad (2)$$

where R is the gas constant, T_o the freezing point of the solvent on the absolute scale, ΔH_o the molecular heat of fusion of the solvent at its melting point, and n' the number of mols of solute in n mols of solvent. This equation, like that of van't Hoff for osmotic pressure, represents only the limit which is approached as the solution becomes more and more dilute. It results from the general equation, as we shall see later, by omitting certain terms which become negligible as the dilution increases.

It is obvious, therefore, that it is scarcely a justifiable procedure

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[18] It is interesting to note in this connection that Berthelot, in 1879, put forward the theory of the existence of hydrates in solution in order to explain certain irregularities in the specific heats of solutions. As his theory in regard to the nature of these complexes is substantially that which is held today, it seems appropriate to call attention here to his views as stated by him thirty years ago. (The italics are mine.)

"Cette diversité et ces inegalitès entre les chaleurs specifiques des dissolutions salines et celles de leurs composants, eau et sel anhydre, paraissent dues, d'après M. Berthelot, à la formation au sein des dissolutions de certains hydrates définis, comparables aux hydrates salins cristallisés; *mais avec cette différence que les hydrates dissous existent le plus souvent au sein de la liqueur dans un état de dissociation partielle, variable avec la quantité d'eau et la température, et suivant des équilibres analogues à ceux des systèmes* éthérés" (*i.e.*, in accordance with the Mass-Action Law. See Mec. Chim. II, 80). [Berthelot, Mecanique Chimique I, 508 (1879)]. Also later, "En résumé, les dissolutions salines doivent être envisagées comme renfermant fréquemment des hydrates salins, tantôt stabiles, tantôt dissociés. Souvent plusieurs de ces hydrates coexistent au sein d'une même liqueur; parfois même ils coexistent avec le sel anhydre, le tout formant un système en équilibre, rigi par les mêmes lois générales que les systèmes homogènes." [Mec. Chim. II, 176.]

to compute the complexity of hydrates in concentrated solutions from the deviations from an equation which strictly represents only the limiting case of the infinitely dilute solution. As an example of the results to which such a calculation has led, a few of the figures obtained by H. C Jones are given below.[19] Jones has applied this equation to the calculation of the approximate composition of the hydrates formed by a large number of substances, both electrolytes and nonelectrolytes, throughout wide ranges of concentration. His calculations in the case of electrolytes also involve the assumption that the degree of ionization is given, at least approximately, by the conductivity ratio. In the following table (Table I) the figures contained in the first three columns are those given by Jones.[20] I have added the last two columns, which follow directly from the content by weight and the specific gravity as given by Jones. It will be noticed from an examination of the figures in the last column that the degree of hydration given by this investigator involves, in all these cases, the "combination" of such a large proportion of the solvent as alone to render the results highly improbable, aside from the fact that the method of calculation is theoretically unjustifiable. When the amount of solvent "combined" amounts in four cases to more than 100 per cent. (as high as 114 per cent. in one instance), it would seem that even this tireless investigator would begin to doubt the validity of his calculations.

TABLE I

Substance.	Mols per liter.	Δt.	Mols of "combined" water per liter of solution.	*Total* mols of water per liter of solution.	Per cent. of water "combined" with solute.
$AlCl_3$	2.0	48.5°	49.03	52.6	93.1
CaI_2	3.1	60.000°	45.8	45.1	101.0
$NiCl_2$	3.5	53.000°	48.9	52.2	93.6
$CuCl_2$	4.4	44.500°	49.77	49.5	100.5
$Cr(NO_3)_3$	1.9	29.500°	44.3	49.1	90.0
H_2SO_4	5.0	76.000°	43.95	43.6	100.8
H_2CrO_4	4.0	57.5°	41.75	36.5	114.0
$C_3H_5(OH)_3$	3.6	36.00°	42.8	45.5	94.0

[19] The work of Jones and his co-workers has been recently collected in a monograph, "Hydrates in Aqueous Solution," Carnegie Inst. Pub. No. 60 (1907).

[20] With the exception of $AlCl_3$, all the values are taken from the above mentioned monograph. The $AlCl_3$ values are from a later publication [Jones and Pearce, Amer. Chem. J., 38, 726 (1907)].

The Fundamental Law of the "Perfect Solution"

Since the law of Raoult for the lowering of the freezing point is applicable only to very dilute solutions, the question naturally arises as to whether there is any general equation for freezing-point lowering which will be valid and give consistent results for solutions of all concentrations. The derivation of such an equation depends upon the law which is to be adopted as the fundamental law for the simplest kind of solution. Such a law must be one which shall be applicable to solutions of all concentrations from zero to infinity. The van't Hoff law for osmotic pressure is obviously not suitable for this purpose, since, as the concentration of a solution increases indefinitely, its osmotic pressure should also increase without limit, a condition which is obviously not consistent with this law.

Now the simplest kind of a solution that can be imagined is a physical mixture in which both constituents exist as simple unpolymerized molecules which do not form complexes with each other. The physical properties of such a solution obey the law of mixtures, being additive with respect to the constituents. A corresponding relation between the activities of the constituents of such a solution is not improbable. Such a relation has been recently proposed by Lewis (see R. 22) as the "criterion of the perfect solution," a perfect solution being by definition one for which this relation holds true. Stated in its most general form, this law is as follows: "At constant temperature and external pressure, the activity, ξ, of each constituent of a perfect solution is proportional to its mol fraction, N, *i.e.*, $\xi = \xi_o N$ (3), ξ_o being the activity in the pure state." By the mol fraction, N, is meant the ratio of the number of mols, n, of the substance in question to the total number of mols, $n + n' + n'' + \ldots\ldots$, of all the substances present in the mixture. For solutions whose vapors obey the laws for mixtures of perfect gases, the activity of any constituent is proportional to its partial pressure, and the law may therefore be stated in the following form: "At constant temperature and external pressure, the vapor pressure, p, of each constituent of a perfect solution is proportional to its mol fraction, N."

This form of the law can be readily tested experimentally. The simplest cases of solution met with in practice are those obtained with the liquid hydrocarbons and many of their substitution products. The process of solution in these cases is not attended by any marked heat

effects or volume changes, and the physical properties of the solution are additive with respect to the constituents. The above vapor pressure law has been tested for many of these solutions and *has been found to hold accurately, for both constituents, over all ranges of concentration from zero to infinity.*[21]

All the evidence available, therefore, seems to justify the conclusion that this law is the best one to adopt as the fundamental law of the simplest type of solution. It is obvious that, for solutions in which polymerization, dissociation, or complex formation takes place, deviations from this law are to be expected. By applying it to such solutions we may therefore hope to obtain some light as to the nature and magnitude of the factors which are responsible for these deviations. In the following pages this law and its thermodynamic derivatives will be applied to the data for aqueous solutions and the results interpreted from the point of view of hydration.

The mathematical expression of the law for each constituent of a binary mixture is

$$p = p_o N \quad \text{and} \quad p' = p'_o N' \tag{4}$$

where p and p' are, respectively, the partial vapor pressures of the two constituents from the mixture, p_o and p'_o their corresponding vapor pressures in the pure state, and N and N', respectively, the mol fraction of each or the number of mols of each in one mol of the mixture. Raoult's law for vapor pressure lowering and Henry's law for the solubility of gases are thus special cases of this law.[22]

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[21] Thus this law has been shown to hold for *both constituents* throughout the whole concentration range for the following pairs of substances:

(1) $CO_2 - CH_3Cl$; (2) $C_6H_{14} - C_8H_{18}$; (3) $C_2H_4Cl_2 - C_6H_6$; (3) $C_2H_4Br_2 - C_3H_6Br_2$; (2) $CH_3OH - C_2H_5OH$; (2) $CH_3COOC_2H_5 - C_2H_5COOC_2H_5$; (2) $C_6H_6 - C_6H_5CH_3$; (4) $C_6H_6 - C_6H_5Cl$; (4) $C_6H_6 - C_6H_5Br$; (2) $C_6H_5CH_3 - C_6H_5C_2H_5$; (4) $C_6H_5CH_3 - C_6H_5Cl$; (4) $C_6H_5CH_3 - C_6H_5Br$; (2) $C_6H_5Cl - C_6H_5Br$.

References:

(1) Kuenen, Z. physik. Chem., **11**, 38 (1893).
(2) Young, J. Chem. Soc., **81**, 768; **83**, 68 (1903).
(3) von Zawidski, Z. physik. Chem., **35**, 129 (1900).
(4) Linebarger, J. Amer. Chem. Soc., **17**, 615, 690 (1895).

[22] This law for the vapor pressures of the constituents of an ideal mixture, and especially the method of expressing concentration in terms of the mol fraction instead of mols per liter, was first used by Willard Gibbs, and has since been consistently used by van der Waals, Duhem, Planck, van Laar, Roozeboom, and others, and is unquestionably the correct method. It has, however, unfortunately not come into general use among chemists, possibly owing to the highly mathematical nature of the treatises of the above writers. See, however, a recent paper by G. N. Lewis, "The Osmotic Pressure of Concentrated Solutions and the Laws of the Perfect Solution" [J. Amer. Chem. Soc., **30**, 668 (1908)], where a more detailed discussion of the question will be found than can be given here. See also the numerous recent papers of van Laar, especially, "The Osmotic Pressure of

The vapor pressure, p, of the solvent from the solution can also be written,

$$p = p_o(1 - N'). \tag{5}$$

Differentiating with respect to N' and substituting for p_o its value, $\frac{p}{1 - N'}$, we obtain the equation,

$$\left(\frac{\partial p}{\partial N'}\right)_T = \frac{-p}{1 - N'}. \tag{6}$$

This equation expresses the change in the vapor pressure of the solvent from a solution at constant temperature, with the change in the mol fraction of the solute.*

Derivation of the Freezing-Point Formula from the General Law of "Perfect Solutions"

If to a mixture of a solid and its liquid at equilibrium a solute be added which dissolves in the liquid but not in the solid, the temperature of the mixture will fall and the vapor pressures p_s and p of solid and liquid, respectively, will be lowered. The lowering of the vapor pressure of the liquid solvent is due to two effects, namely, to the effect

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Solutions of Non-Electrolytes with Reference to the Deviations from the Laws of a Perfect Gas" [Proc. K. Akad. Wet. Amsterdam, **21**, 53 (1906)] and "Sechs Vorträge über das Thermodynamische Potential," etc.; "Zwei Vorträge über nichtverdünnte Lösungen und über den Osmotischen Druck" [Braunschweig, Friedrich Vieweg und Sohn 1906], where the thermodynamics of solutions is treated from the standpoint of the Gibbs thermodynamic potential function and the general laws of solutions, both dilute and concentrated, are developed.

* Note added September 10. In a recent publication [Z. physik. Chem., **63**, 641, August (1908)], Callendar adopts the equation,

$$\frac{p_o - p}{p_o} = \frac{n'}{n},$$

as the fundamental law for concentrated solutions, n' being the number of mols of solute in n mols of solvent. He applies this equation and its thermodynamic derivatives to the data for aqueous solutions and interprets the results from the point of view of hydration. This equation, however, ike the van't Hoff law for osmotic pressure and the Raoult freezing-point equation, must be regarded as strictly applicable only to dilute solutions, its application as a general law for solutions of all concentrations being unjustified. This is readily seen when the equation is written in the form,

$$p = p_o\left(1 - \frac{n'}{n}\right).$$

For a fifty mol per cent. solution, this equation requires that the vapor pressure of the solvent shall be equal to zero and that for higher concentrations it shall be negative.

of the solute and to the lowering of the temperature; or in mathematical terms, if dN' mols of solute be added to 1 mol of a solvent in equilibrium with its solid phase,

$$dp = \left(\frac{\partial p}{\partial N'}\right)_T dN' + \left(\frac{\partial p}{\partial T}\right)_{N'} dT. \tag{7}$$

The change in vapor pressure of the solid is given by the equation,

$$dp_s = \left(\frac{\partial p_s}{\partial T}\right) dT. \tag{8}$$

Since the solid and the solution are kept in equilibrium, $dp = dp_s$, and we have by combining equations (7) and (8),

$$\left(\frac{\partial p_s}{\partial T}\right)_{N'} - \left(\frac{\partial p}{\partial T}\right)_{N'} = \left(\frac{\partial p}{\partial N'}\right)_T \frac{dN'}{dT}. \tag{9}$$

For the influence of temperature on the vapor pressure of a liquid or solid when the total pressure is constant, it can be readily shown[23] that the following equations are rigorously exact.

$$\left(\frac{\partial p_s}{\partial T}\right)_{N'} = \frac{L_s}{VT}, \tag{10}$$

$$\left(\frac{\partial p}{\partial T}\right)_{N'} = \frac{L}{VT}, \tag{11}$$

where L_s and L are respectively the molecular heats of vaporization of solid and liquid under constant pressure, and V is the molecular volume of the vapor at the temperature T. Subtracting these two equations, we obtain,

$$\left(\frac{\partial p_s}{\partial T}\right)_{N'} - \left(\frac{\partial p}{\partial T}\right)_{N'} = \frac{L_s - L}{VT} = \frac{\Delta H}{VT}, \tag{12}$$

where ΔH is the molecular heat of fusion of the solvent into the solution at the temperature T. Substituting this result in equation (9) and combining with (6), we obtain,

$$\frac{dN'}{dT} = \frac{-\Delta H(1 - N')}{PVT}. \tag{13}$$

Substituting $RT = PV$ in (13) and putting $T = T_o + t$ where T_o is the absolute temperature of the freezing point of the pure solvent, we have

[23] See Lewis, Proc. Amer. Acad., 37, 53 (1901).

$$\frac{dN'}{dt} = \frac{-\Delta H(1 - N')}{R(T_o + t)^2}. \tag{14}$$

In order to integrate, it is only necessary to express ΔH as a function of the temperature.

We shall consider now that we are dealing with water solutions. If ΔH_o is the molecular heat of fusion of ice at 0° and ΔC_p the difference between the molecular heat capacities of ice and water, respectively, at constant pressure, we have the well-known relation,

$$\Delta H_t = \Delta H_o + \Delta C_p t, \tag{15}$$

assuming ΔC_p constant. Making this substitution we have for the final form of the differential equation,

$$\frac{dN'}{dt} = \frac{-(\Delta H_o + \Delta C_p t)(1 - N')}{R(T_o + t)^2}. \tag{16}$$

Integrating in the usual manner and evaluating the integration constant by noting that when $N' = 0$, $t = 0$, we obtain,

$$\ln(1 - N') = \frac{\Delta C_p}{R} \cdot \ln\frac{(T_o + t)}{T_o} - \frac{\Delta H_o + \Delta C_p t}{R(T_o + t)} + \frac{\Delta H_o}{RT_o}. \tag{17}$$

This form of equation is not convenient to use in practice, however. A simpler form is obtained if the integration is performed by use of Maclaurin's theorem, which can be applied directly to the differential equation, since when $N' = 0$, $t = 0$. Integrating in this manner and retaining only two terms [24] in the series, we obtain

$$N' = \frac{\Delta H_o}{RT_o^2}\left[\Delta t - \frac{1}{2}\left(\frac{\Delta H_o}{RT_o^2} + \frac{\Delta C_p}{\Delta H_o} - \frac{2}{T_o}\right)\Delta t^2\right], \tag{18}$$

where for $-t$ is written Δt, the freezing-point lowering. In the case of water the constants have the following values: [25]

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[24] Two terms are sufficient, in the case of water, for all freezing-point lowerings of not more than 7°, assuming an accuracy of 0.001° in the measurements. For lowerings of more than 7° the third term in the expansion should be included.

[25] These values are taken from the most accurate data available. The value of ΔH_o is calculated from the excellent data of A. W. Smith [Phys. Rev., **17**, 193 (1903)], using the latest value for the potential of the Standard Clark Cell at 15°, *i. e.*, 1.433 volts [see Guthe, Bull. Bureau Stands., **2**, 69 (1906)].

The specific heat of water is taken as 1.0 cal. and that of ice as 0.50 cal. [Bogojawlenski, Chem. Centrbl. II, 946 (1905)]. The value of T_o is that adopted by Buckingham as a result of a careful consideration of all data available [see Bull. Bureau Stands., **2**, 273 (1907)]. The value for R is that given by Berthelot [Z. Electrochem., **10**, 621 (1904)].

ΔH_o . . .	6009.8	Joules
ΔC_p . . .	36.8	Joules per degree
R . . .	8.3162	Joules per degree
T_o . . .	273.13°	

Substituting these values in equation (18), we obtain for the relation between the mol fraction N' of the solute and the lowering of the freezing point (Δt) in water solution the equation:

$$N' = 0.0096895(\Delta t - 0.00425\Delta t^2) \qquad (19)$$

Application of the Freezing-Point Equation

In order to test this equation for water solutions all the available data on the freezing points of concentrated aqueous solutions of non-electrolytes were collected, and the values of Δt were plotted against the corresponding values of the mol per cent., $100N'$, in each case. The curves for all the substances were plotted on a large scale, together with the theoretical curve. It was found that the experimental curves for the various substances were about equally distributed on both sides of the theoretical curve, and *that, with but few exceptions, all the curves converged into the theoretical curve in the neighborhood of a concentration of 1 mol per liter.*

The complete set of curves on one plot cannot be reproduced without too great a sacrifice of detail, owing to the necessary reduction in size. The points for concentrations from zero up to about twice molal are, however, shown in the accompanying figures. As is evident from these figures, very few accurate data on the freezing points of concentrated aqueous solutions are available. The results of Raoult for ethyl alcohol and those of Raoult and of Ewan for cane sugar are among the few examples of accurate experimental work on concentrated solutions. The heavy line in each figure is the plot of the theoretical equation.

The data on freezing points are by the following observers:[26] Loomis (L), Abegg (A), Jones (J), Roth (R), Raoult (Ra), Ewan (E), Morse and Frazer (M and F).

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[26] Loomis, Z. physik. Chem., **32**, 591 (1900); **37**, 414 (1901). Abegg, Z. physik. Chem. **15**, 218 (1894). Jones, R. 19. Roth, Z. physik. Chem., **43**, 560 (1903). Raoult, Z. physik. Chem., **27**, 646 (1898). Ewan, Z. physik. Chem., **31**, 27 (1899). Morse and Frazer, Amer. Chem. J., **34**, 1 (1905); **37**, 324, 425, 558; **38**, 175 (1907).

Figure 2. — The data for these substances show no systematic variations from the theoretical curve.[27]

Figure 3. — No systematic variations are apparent except perhaps in the case of ethyl formate.[28]

Figure 4. — In the case of the alcohols it is to be noted that the accurate data of Raoult for ethyl alcohol show almost exact agreement with the theoretical curve. The variations in the case of the other alcohols are within the probable experimental errors of the data. In the case of glycerin the three widely deviating points are from the data of Jones and Getman. These results led Jones to conclude that glycerin possesses, to a remarkable degree, the tendency to form hydrates of high molecular weight. These results are, however, probably in error by more than 100 per cent., since the data of the other observers (*i.e.*, Loomis, and Abegg) exhibit no such deviation from the theoretical curve. On the contrary glycerin appears to be quite a normal substance as far as its effect on the freezing point is concerned.[29]

Figure 5. — The data for levulose and dextrose show decided variation from the theoretical, the deviations being such as would be produced if the solute were hydrated.[30]

In connection with the results obtained by Roth for glucose one point is worthy of mention. Roth found that freshly prepared solutions of glucose gave smaller values for the molecular lowering than did the same solutions after standing a few days. The increase in the molecular lowering with the time corresponded to the decrease in the birotation. Hydration has been suggested as a possible explanation of this result, and this is probably the true explanation. A similar slowly progressing hydration, accompanied by a corresponding change in the optical rotation, has been studied in the case of milk sugar and will be discussed later (page 393).

Figure 6. — This shows the data for glycocoll and cane sugar,[30a] both

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[27] Counting from the origin the points are by the following observers: $CO(NH_2)_2$, J. CH_3CONH_2, 1, 2, 4, L; 3, 5, J. $CCl_3COH.H_2O$, 1, 2, 3, 4, 5, 7, 8, 10, R; 11, A; 6, L; 9, 12, J.

[28] CH_3COCH_3, 1, 3, L; 2, A. All others, A.

[29] Points in Figure 4 are: CH_3OH, 1, L; 2, 3, J; 4, 5, A. C_2H_5OH, 1, 3, 4, 6, 7, Ra; 2, L; 5, J. C_3H_7OH, 1, L; 2, 3, J; 4, A.

[30] Levulose, J. Lactose, 1, L; 3, 5, Hudson (see this review, page 393); 4, 6, J. Dextrose, 1, 2, 3, 5, 6, 7, 9, J; 4, 8, 10, R. Mannite, 1, 2, J; 3, L.

[30a] The data for glycocoll are by Roth, and those for sugar by Loomis, Morse and Frazer, Raoult, and Ewan.

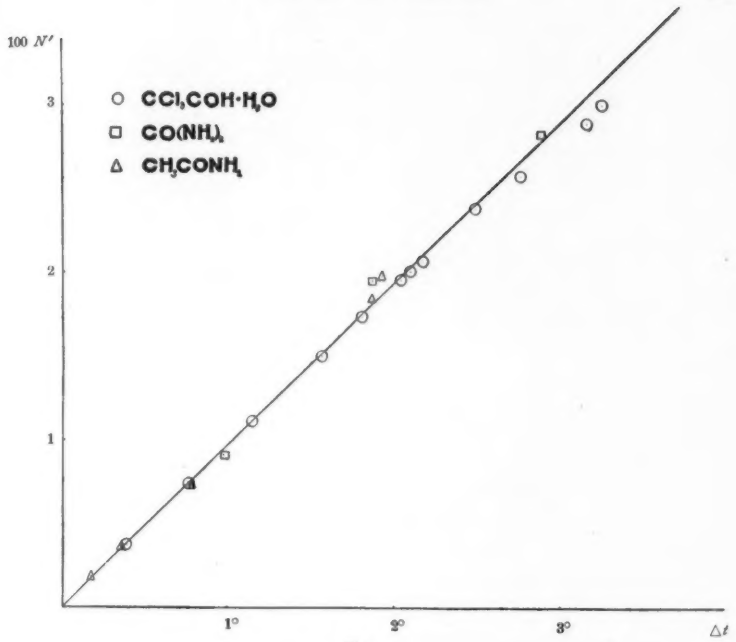
100 N'
3
2
1
○ CCl₃COH·H₂O
□ CO(NH₂)₂
△ CH₃CONH₂
1°
2°
3°
Δt

FIG. 2

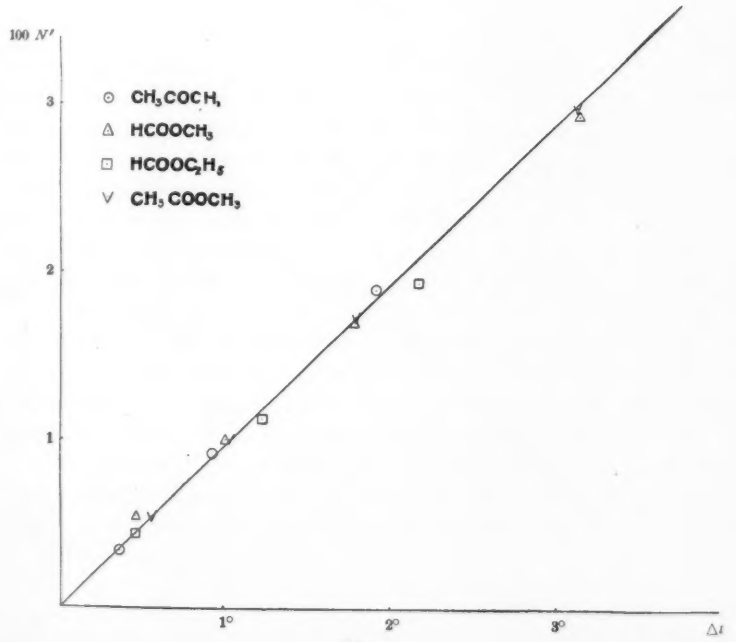
100 N'
3
2
1
⊙ CH₃COCH₃
△ HCOOCH₃
□ HCOOC₂H₅
▽ CH₃COOCH₃
1°
2°
3°
Δt

FIG. 3

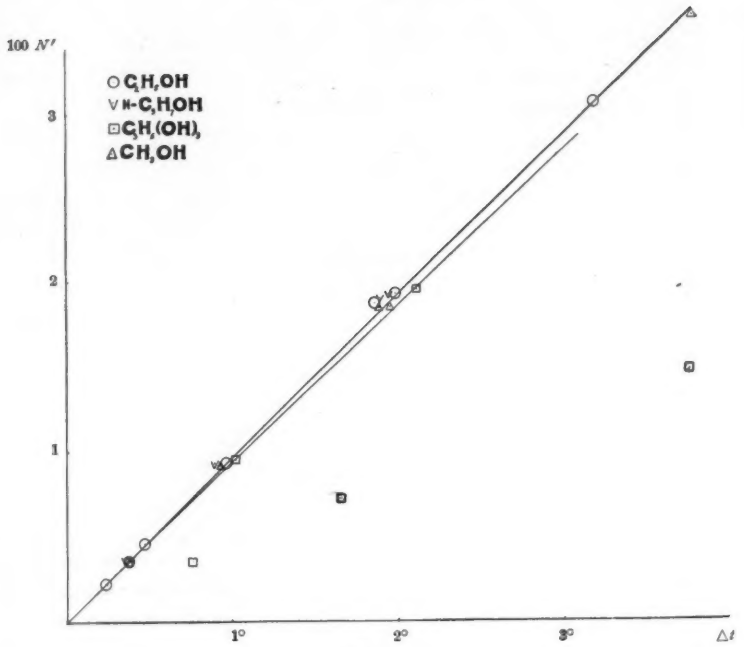
100 N'
○ C_2H_5OH
∨ n-C_3H_7OH
□ $C_3H_5(OH)_3$
△ CH_3OH
3
2
1
1°
2°
3°
Δt

FIG. 4

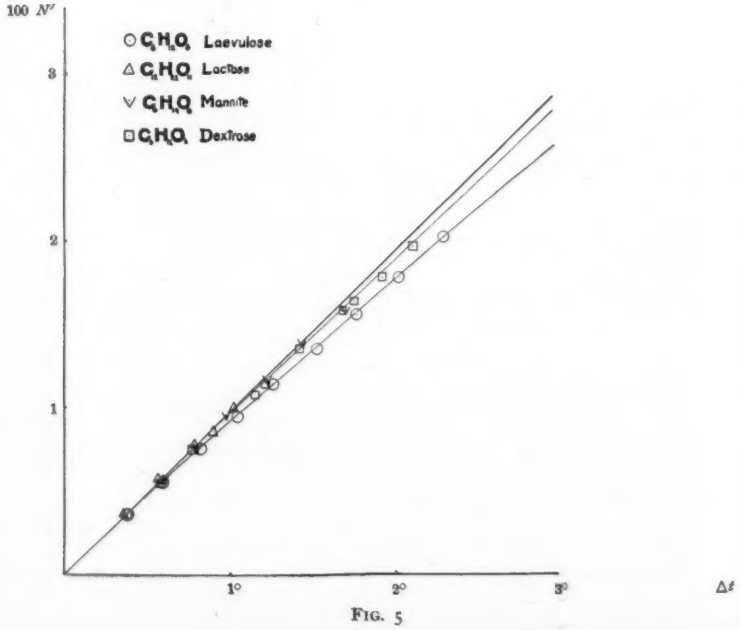
100 N'
○ $C_6H_{12}O_6$ Laevulose
△ $C_{12}H_{22}O_{11}$ Lactose
∨ $C_6H_{14}O_6$ Mannite
□ $C_6H_{12}O_6$ Dextrose
3
2
1
1°
2°
3°
Δt

FIG. 5

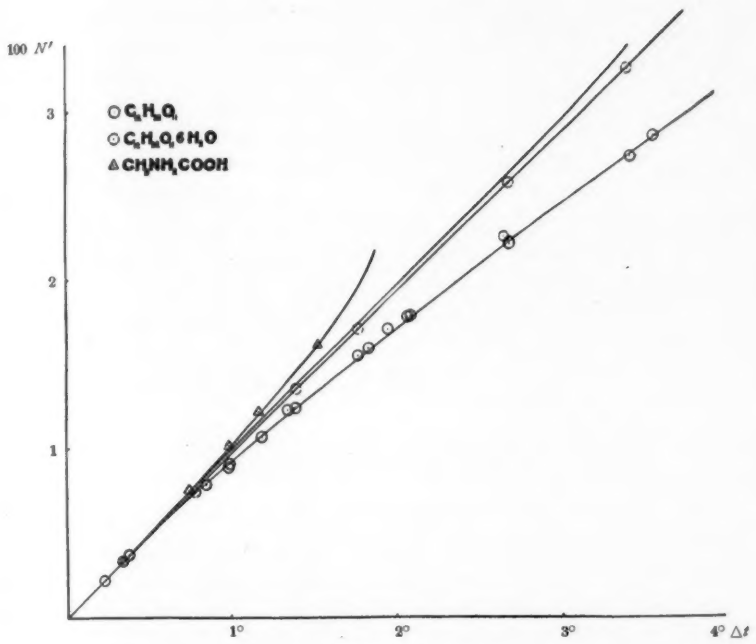

FIG. 6

of which deviate decidedly from the theoretical curve. In the case of the former the deviation is in the direction which would result if the solute were partially associated into double molecules, a result which is more or less to be expected in the case of an amphoteric substance of the nature of amidoacetic acid. The deviation in the case of cane sugar is in the direction which would result from hydration. The dotted circles represent the values obtained for cane sugar if the assumption is made that it exists in solution as the hydrate $C_{12}H_{22}O_{11}\cdot 6H_2O$. This assumption gives values agreeing almost exactly with the theoretical curve. The assumption of the hydrate $C_{12}H_{22}O_{11}\cdot 7H_2O$, on the other hand, gives values lying along the line on the opposite side of the theoretical curve. Beyond twice molal the curve for the hexahydrate begins to deviate again from the theoretical, lying below it.

The foregoing consideration of the freezing-point method shows clearly that if this method is to have any value for the quantitative study of hydration in solution, a formula like that here proposed,

which seems to apply through a considerable range of concentration, to normal, probably anhydrous substances, must be employed, and the application even of this formula must be confined to the region of not too concentrated solutions, say up to twice molal. If this method is to be applied to solutions of electrolytes, the measurements should be confined to solutions preferably in the neighborhood of 0.5 to 0.7 molal, where the degree of ionization as determined by the conductivity ratio may be regarded as at least approximately correct. We are, however, not yet in possession of sufficient accurate data in this region to attempt a quantitative interpretation of the results. If it could be shown that the freezing-point data for some electrolytes (perhaps $CsNO_3$)[30b] fitted the theoretical curve, it would increase greatly the probability that the hydration calculations in the case of the widely deviating ones were somewhere near the truth.

The Boiling-Point Method

The curves showing the relation between the "molecular elevation" of the boiling point and the concentration in mols per 1,000 grams of water exhibit, in many cases, minima similar to those found in the corresponding freezing-point curves, but they are in general much less pronounced.[30c] The relative positions of the minima for different salts with the same anion occur in the same order as the corresponding freezing-point minima, but at greater concentrations in the former than in the latter case. It has been pointed out by Biltz (R. 15, p. 221) and by Jones and Getman (R. 16, p. 343) that this fact would seem to indicate that the complexity of the hydrates in solution decreased with rising temperature, a conclusion which is in accordance with the fact that the complexity of solid crystalline hydrates decreases with rise in temperature. It is also borne out by certain other facts, especially the heats of dilution, as will be pointed out later (page 380).

As in all the other methods of measuring changes in the activity of the solvent, the boiling-point results for concentrated solutions *should not be interpreted by means of a law of the infinitely dilute solution*, as is usually done. By a perfectly analogous method to that used in

[30b] Some results obtained by Biltz (R. 15, p. 218) on the freezing points of some cæsium nitrate solutions indicate that the data for this salt may possibly fit the theoretical curve. A study of freezing points and corresponding conductivities of moderately concentrated solutions of cæsium nitrate will be undertaken shortly by the reviewer.

[30c] See Biltz, R. 15, p. 209; Smits. Z. physik. Chem., **39**, 419 (1902); also S. M. Johnson, Trans. Roy. Soc. Ed., **45** [I], 193 (1907).

deriving the freezing-point formula, a general boiling-point formula for solutions of all concentrations can be derived, based upon the simple assumption that the activities of solute and solvent are proportional to their respective mol fractions. It would, however, unduly lengthen this paper to treat this method in detail, as was done in the case of the freezing-point method. Accurate boiling-point data are, moreover, very rare, a few results obtained by Smits (R. 32, p. 418) being the only ones that I have been able to find which approach the accuracy necessary for a quantitive treatment. The method itself is not as satisfactory either from an experimental or a theoretical standpoint as the vapor-pressure method, which will next be considered.

The Vapor–Pressure Method

Of all the methods of studying hydration in solution, which depend upon changes produced in the activity of the solvent, the method of vapor-pressure lowering is, in general, greatly to be preferred. Being an isothermal method, its thermodynamic treatment is very simple and does not involve the necessity of knowing the values of numerous physical constants, such as the gas constant, heat capacities, heat effects accompanying changes in state, etc., an accurate knowledge of which is necessary in using the equations of the freezing and boiling point methods. It has the further advantage that it can be readily applied over a wide range of temperature and, with proper precautions, it is capable of a high degree of accuracy even at low temperatures. Moreover, the relative degrees of hydration for different concentrations of the solute as calculated from vapor-pressure measurements are directly comparable with one another, since they may all be determined at the same temperature. The results obtained by the freezing-point method, on the other hand, are never directly comparable with one another, since they all correspond to different temperatures, namely, the freezing point of the solution in each case.

This important fact, which seems to have been entirely overlooked by investigators using this method, may well be the explanation of certain results obtained with the strong acids which were apparently contradictory to the Mass-Action Law. The Mass-Action Law requires that the degree of hydration of a given molecular species in solution shall increase with the dilution *at constant temperature*. Jones and Pearce (R. 20, p. 729) found that in the case of the strong acids, HCl,

HNO_3, and H_2SO_4, the freezing-point data seem to indicate that the average molecular hydration of the solute is *increasing* with the concentration. This led these investigators to conclude that hydrates in these cases exist only in concentrated solutions, the assumption being made that only the undissociated molecule possesses the power to form hydrates. This assumption, which was apparently made solely for the purpose of explaining a behavior which it was thought would otherwise constitute a contradiction to the Mass-Action Law, is not at all probable and is not borne out by other facts (R. 100*a*, p. 319). It would indeed not be surprising to find that in the case of the strong acids the degree of hydration *at the freezing point of the solution* should increase with the concentration. These acids possess rather large positive heats of dilution, the greater part of which may well represent heat of hydration; consequently the degree of hydration would increase with falling temperature, and it is therefore rather to be expected that twice molal sulphuric acid, for example, should show a greater average molecular hydration at its freezing point (− 11°) than the molal acid at its freezing point (− 4°), although at constant temperature the change should be in the opposite direction.

In order to render results obtained by the freezing-point method directly comparable with one another, it is necessary to refer them all to the same temperature, preferably 0°. This could be most conveniently done by calculating, thermodynamically, the vapor pressure of each solution at 0° from the observed depression of the freezing point. Such a calculation involves, however, a knowledge of the heat of dilution at 0°, and also possibly of its temperature coefficient if the calculation involved any considerable temperature interval.[31]

The vapor-pressure lowering, Δp, for the perfect solution, is given by the equation,

$$(\Delta p) = p_o N', \qquad (20)$$

[31] Errors due to the failure to appreciate the fact that all results obtained by freezing-point methods refer not to zero degrees but to the freezing point of the solution in each case are not uncommon. Thus Smits [Z. physik. Chem., **39**, 424 (1902), and **51**, 40 (1905)], using a formula of van Laar's connecting vapor-pressure lowering and freezing-point lowering,

$$\left[\left(\frac{\Delta p}{p_o}\right) + \frac{1}{2}\left(\frac{\Delta p}{p_o}\right)^2 = \Delta t \frac{\Delta H_v}{R t_o^2} \cdot \frac{T_o}{T}\right],$$

calculates the values of Δp for concentrated solutions from the freezing-point data, and compares them with his own directly measured values at *zero degrees* with "gut Übereinstimmung." Agreement is not to be expected except for solutions with negligible heats of dilution, since the values of Δp obtained by the above formula refer not to zero degrees but to the freezing point of the solution.

which follows directly from equation (4). The application of this equation involves the knowledge of but one constant, p_o, the vapor pressure of pure water at the temperature in question. The necessary data for applying the above equation to water solutions for the purpose of calculating the composition of hydrates are not at present available. The most accurate vapor-pressure measurements in moderately concentrated solutions appear to be those of Smits,[31] all at 0°, which were determined by a differential statical method. He investigated solutions of NaCl, H_2SO_4, KNO_3, and $C_{12}H_{22}O_{11}$. In the case of the first two substances, minima in the values of the molecular lowering of the vapor pressure occur at about 0.5 molal concentration. To illustrate the method of calculating the degree of hydration from vapor-pressure data we will apply the formula to Smits' data for cane sugar at 0°.

We have as the general expression for a perfect solution:

$$\frac{\Delta p}{p_o} = \frac{n'(1+\gamma)}{(1+\gamma)n' + n}. \tag{21}$$

For a nonelectrolyte $\gamma = 0$, and therefore

$$n = \frac{n'p_o}{\Delta p} - n'. \tag{22}$$

For a sugar solution containing 1.0089 mols of sugar per 1,000 grams of water, Smits found $\Delta p = 0.09125$ mm. Assuming $p_o = 4.579$ mm. (Landolt and Börnstein), the above equation gives $n = 49.8$. The total number of mols of water present being $\frac{1000}{18} = 55.5$, the difference, 5.7 mols, represents the average molecular hydration which must be assumed if the deviation from the law of the perfect solution is to be attributed to hydration. This substantial agreement with the value obtained from the freezing-point data, 6.0 mols, is a verification of the experimental data (since neither the difference in temperature nor the heat of dilution is large), but not a theoretically independent confirmation of the conclusion that sugar exists in solution as a hexahydrate.

The Method of Solubility Lowering

The phenomenon of solubility lowering, or the "salting-out" effect, as it is frequently called, has received considerable attention at the hands of investigators, and several theories have been advanced to explain it. We shall confine our attention in the present discussion

to its bearing upon the hydrate problem. Euler[32] has suggested that the "salting-out" effect is to be regarded as a function of the internal pressure (Binnendruck) of the solution. This view is also supported by Geffcken[33] in his critical review of the subject. Rothmund[34] has advanced the hypothesis that the "salting-out" effect is primarily due to a combination between the "salting-out" substance and a portion of the solvent, thereby diminishing the amount of "free" solvent present and hence lowering its solvent power. Levin,[35] however, combats both hypotheses, maintaining that the true explanation is to be found in the mutual action of the two solutes upon each other.

It will be noticed at once that in studying a "salting-out" effect we have always to deal with a ternary system. It is this fact which renders this method so difficult to treat satisfactorily from a thermodynamic standpoint. Accurate differential equations can be set up, it is true, but they cannot in general be integrated. For example, consider a system consisting of N' mols of a solute, s', and N'' mols of a second solute, which we will call for convenience the "salting-out" substance, s'', dissolved in N mols of water, $N' + N'' + N$, being equal to 1. If we increase the number of mols of any constituent, say the substance s'' in the solution, the resulting changes in the activities of all the constituents of the mixture can be shown[36] to be connected by the equation,

$$\left(\frac{N'\partial ln\xi' + N''\partial ln\xi'' + N\partial ln\xi}{\partial N''}\right)_{P,T,} = 0. \qquad (23)$$

This is all that pure thermodynamics will tell us about the changes taking place in such a system. If the solution is saturated with the solute, s', its activity is thereby kept constant and $\partial ln\xi' = 0$, so that the equation becomes

$$\left(\frac{N''\partial ln\xi'' + N\partial ln\xi}{\partial N''}\right)_{P,T,} = 0. \qquad (24)$$

[32] Euler, Z. physik. Chem., **31**, 368 (1899).

[33] Geffcken, Z. physik. Chem., **49**, 287 (1904). For relations between solubility lowering and other physical properties of solutions, such as compressibility and surface tension, see a recent paper by Ritzel. [Z. physik. Chem., **60**, 319 (1907)].

[34] Rothmund, Z. physik. Chem., **33**, 413 (1900).

[35] Levin, Z. physik. Chem., **55**, 530 (1906).

[36] See Lewis, Proc. Amer. Acad., **55**, 530 (1906).

If the concentration of the substance, s'', is sufficiently low, so that the criterion of the perfect solution can be applied to it, we have (see p. 368)

$$\xi'' = \xi''_{\circ} N''.$$

Taking the logarithm of both sides and differentiating, we obtain

$$\partial ln\xi'' = \partial lnN'',$$

which on substitution in equation (24) gives

$$N dln\xi = - dN'',$$

$$\text{or} \quad dln\xi = \frac{d\xi}{\xi} = - \frac{dN''}{N}, \tag{25}$$

an equation first obtained by Lewis (R. 36, p. 279). For the case that the vapor of the solvent obeys Boyle's law, this becomes

$$\frac{dp}{p} = - \frac{dN''}{N},$$

$$\text{or} \quad \left(\frac{\partial p}{\partial N''}\right)_T = - \frac{p}{N},$$

which is identical with equation (6) for a binary system. Stated in words, this means that the addition of a solute to a saturated solution of any substance, s', produces the same lowering in the vapor pressure of the solvent as would be produced if it were added to the same amount of solvent in the pure state.

This conclusion, of course, assumes that no complex formation occurs between the two solutes. Obviously, therefore, so far as the study of the change in the activity of the solvent is concerned, there is no advantage in having the solute, s', present, but rather a disadvantage, since it always introduces the possibility of a mutual action between the two solutes. It is because of this possibility that a three component system is so poorly adapted to the study of the relations between any two of the components. In fact, an examination of the numerous data on the "salting-out" effect shows that, *in general*, the results cannot be explained on the simple assumption of mutual action between solvent and "salting-out" substance. Action between solute and "salting-out" substance also enters to a greater or less degree, depending upon the nature of the two solutes.

Levin (R. 35, p. 528) seems inclined to regard this latter effect as the whole explanation, abandoning the hydrate hypothesis entirely. His

argument, which is also that previously advanced by MacLauchlan,[87] is as follows: "Soll also die Hydrattheorie zur Erklärung der Löslichkeitsbeeinflussung herangezogen werden, so dürfen die in Betracht kommenden Lösungen nicht mehr als, 'verdünnte' gelten. Da aber die hier zur Diskussion herangezogenen Konzentrationen immerhin nicht sehr hohe sind, so scheint es erlaubt, zur Gewinnung eines angenähert richtigen Resultats die Gesetze der verdünnten Lösungen anzuwenden, im besondern das Massenwirkungsgesetz und den von Nernst bewiesenen Satz, dass die aktive Masse des Wassers seinem Dampfdrucke proportional ist. Die einfachste Vorstellung, die man sich von dem Einfluss einer Hydratisierung auf die Löslichkeit bilden kann, ist folgende. Infolge der Hydratbildung der ersten Substanz steht dem zweiten Stoff weniger Lösungsmittel zur Verfügung, seine Löslichkeit sinkt. Nun beträgt die Dampfspannungserniedrigung in normalen Lösungen starker Elektrolyte etwa 4%, um ebensoviel nimmt nach dem Nernstschen Satze die aktive Masse des Wassers ab, während bei gleicher Konzentration die Löslichkeitsbeeinflussung durch starke Elektrolyte im Durchschnitt etwa 20% beträgt. Diese Erklärungsweise ist daher nicht anwendbar, worauf bereits MacLauchlan hingewiesen hat." This argument, however, contains the tacit assumption that the solvent power of a solvent is proportional to its active-mass as measured by its vapor pressure, an assumption which seems scarcely justified.

If the "salting-out" method is to be of any value for the calculation of the complexity of hydrates in solution, the following condition must obviously be fulfilled: the solubility, S, of a solute in a water solution is proportional to the number of mols, N_w, of "free" water which are present in the solution, that is,

$$S = S_o N_w, \tag{26}$$

S_o being its solubility in 1 mol of pure water. Under this assumption the degree of hydration can be calculated for any case from the deviations experimentally found. Unfortunately for the purposes of studying hydration, this assumption is found to be the exception rather than the rule.

A few examples will serve to illustrate the results obtained when this method is applied to the study of hydration. We have already seen (Fig. 2, p. 375) that freezing-point data indicate that chloral

[87] MacLauchlan, Z. physik. Chem., 44, 624 (1903).

hydrate in aqueous solution is a "normal" substance, and therefore presumably not hydrated Its presence in solution in moderate concentration should therefore not affect the solubility of a second solute with which it does not combine in any way. This is, in fact, found to be the case for hydrogen, as shown by the following table, which has been calculated by Philip[38] from the data of Knopp.[39].

TABLE II

Per cent. of chloral hydrate.	c.c. of H_2 dissolved by 100 grams of H_2O.
0.0	18.83
4.91	18.95
7.69	18.92
14.56	18.78
18.77	18.69
29.5	19.07

We have seen (Fig. 6, p. 377) that the freezing-point and vapor-pressure experiments with cane sugar solutions indicate a hydration of about 6 mols of water to 1 of cane sugar. From Steiner's[40] results on the solubility of hydrogen in cane sugar solutions Philip has computed the following table:

TABLE III

Per cent. of sugar.	c.c. of H_2 dissolved by 1,000 grams of H_2O at 15°.	Average molecular hydration of sugar.
0.00	18.83	. .
16.67	17.55	6.5
30.08	16.27	6.0
47.65	13.95	5.4

The figures in the last column show that the presence of each mol of cane sugar in the solution has the same effect on the solubility of hydrogen as would result by the removal of 6 mols of water. So far the results seem to be in complete agreement with those given by the

[38] Philip, Trans. Far. Soc., 3, 141 (1907).

[39] Knopp, Z. physik. Chem., 48, 97 (1904).

[40] Steiner, Wied. Ann., 52, 275 (1894).

previously discussed methods. When we turn to electrolytes, however, the agreement ceases to exist. In the following table are given the results obtained for three electrolytes from the data of Steiner on the solubility of hydrogen in aqueous salt solutions at 15°. From these results it would appear that lithium chloride is the least hydrated of these chlorides, while all other methods unite in giving it the highest hydration.

TABLE IV

Solute.	Mols of salt per 1,000 grams of H_2O.	c.c. of H_2 per 1,000 grams H_2O.	"Average molecular hydration" of the solute.
KCl	0.500	17.30	9.0
	0.956	16.09	8.5
	1.51	14.54	8.4
	2.28	12.54	8.1
	2.65	11.56	8.1
NaCl	0.740	16.20	10.5
	1.75	12.70	10.3
	2.28	10.84	10.3
	3.45	7.80	9.5
LiCl	0.804	16.78	7.5
	1.65	14.78	7.2
	3.18	11.60	6.7

The order in which the "salting-out" power of the various ions increases is, according to Rothmund,

Cations, NH_4, Cs, Li, Rb, K, Na;
Anions, NO_3, I, Br, Cl, SO_4.

This order is approximately independent of the nature of the nonelectrolyte which is being salted out. This fact would indicate that the "salting-out" effect in these cases is due to some action of the "salting-out" substance upon the solvent rather than upon the solute. This conclusion is further strengthened by the fact, first shown by Rothmund,[34] that in many cases the heat of solution of the solute in the salt solution is the same as that in pure water, which would not in general be the case if a reaction occurred between the solute and the "salting-out" substance. It will be noticed that the order of the ions as given above is *not* that obtained from the freezing-point and other data (see

pages 364 and 412), which clearly shows that if hydration is assumed to account for the solubility lowering it is complicated by other effects. Furthermore the above order is not perfectly general, some exceptions being known.

In addition to the above mentioned attempts to calculate hydration from the "salting-out" effect, some recent work of Armstrong[41] and others may be mentioned.[42] Armstrong studied the "salting-out" action of ethyl alcohol and hydrochloric acid on aqueous solutions of the haloid salts of the alkali metals at 25° and calculated the "apparent molecular hydrations" of the two precipitants by the above principle. The results for ethyl alcohol, for example, varied from $-.64$ to 4.2 mols of water, according to the concentration and the salt which was being salted out. It is scarcely necessary to say that whatever these values may represent they do not represent hydration. Armstrong has also collected all the data on the "salting-out" effect and calculated the "average molecular hydration" of a number of acids, salts, and bases.

In connection with the discussion of this method, the action of salts on the separation of a solution into two phases may be mentioned. Smirnoff[43] has studied this phenomenon in the case of isobutyric acid and water. The method of investigation consisted in determining the temperature at which different amounts of the salt in question caused the solution to become cloudy, owing to the separation of the isobutyric acid. He found that the effect of the cations increased in the series, Cs, Rb, NH_4, K, Na, Li, Cd, Ba, Sr, Ca, Mg, Al, and the anions in the series, NO_3, Br, $\frac{1}{2}SO_4$, Cl. It will be noticed that here the order of the cations is the same as that for their effect on the freezing point, boiling point, etc., as previously discussed[44] (page 364). Smirnoff attributes the result to the hydration of the salts in solution.

Distribution of a Solute between a Solvent and a Second Nonmiscible Phase

This method will, for convenience of treatment, be divided into three divisions, *A*, *B*, and *C*. Under division *A* will be discussed the

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[41] Armstrong, Proc. Roy. Soc., London, **79**, 567, 586 (1908).

[42] For a complete list of references to the literature on the "salting-out" effect see R. 33 and R. 35.

[43] Smirnoff, Z. physik. Chem., **58**, 667 (1907).

[44] In this connection see also the work of Timmermans on the critical solubility temperatures of ternary mixtures. Z. physik. Chem., **58**, 129 (1907).

limiting case where the second nonmiscible phase is the pure solid or liquid solute. This case comprises, therefore, the general phenomenon of solubility of a substance in water and its bearing upon the problem of hydration. Division *B* will deal with a peculiar case of solubility, where the solute exhibits what is called a "maximum rate of solution." The case where the second nonmiscible phase is a liquid or a gas will be treated in division *C*.

A. Solubility-Temperature Curves. — From the general form of the solubility-temperature curves of certain substances in aqueous solution, information regarding the extent of hydration in the solution can

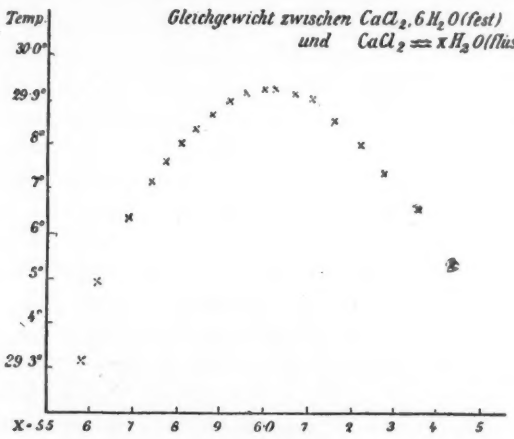

FIG. 7

be obtained. Of especial interest in this respect are the solubility curves of crystalline hydrates, many of which have been investigated. A good illustration of this type of curve is found in the case of $CaCl_2 \cdot 6H_2O$, first investigated by Roozeboom.[45] This curve, which has been carefully determined by Lidbury,[46] is shown in Figure 7. Temperatures are plotted as ordinates, and mols of H_2O per mol of $CaCl_2$ in the liquid phase as abscissæ. As shown by the form of the curve, the solubility of $CaCl_2 \cdot 6H_2O$ in water increases gradually with the temperature, reaching a maximum at 29.92° and then gradually decreasing.

[45] Roozeboom, Z. physik. Chem., 4, 32 (1889).

[46] Lidbury, *ibid.*, 39, 460 (1902).

The first branch of the curve corresponds to a liquid phase containing more, the second branch to one containing less than 6 mols of H_2O per mol of $CaCl_2$. At the vertex the liquid has the same composition as the solid, and this point, therefore, represents the melting point of $CaCl_2 \cdot 6H_2O$.

The effect of the degree of hydration in the liquid phase upon the shape of the solubility curve will be most readily understood by a consideration of the effect of the addition of either $CaCl_2$ or H_2O to the liquid in contact with solid $CaCl_2 \cdot 6H_2O$ at its melting point. Two lim-

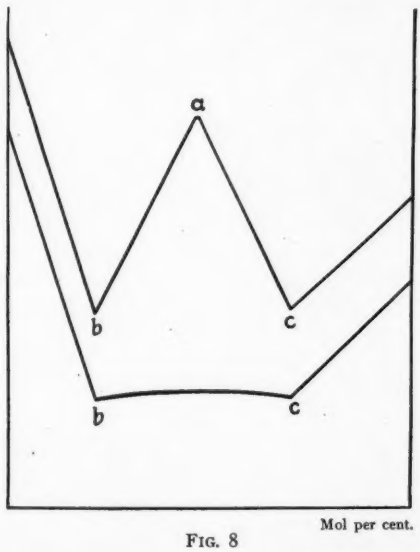

FIG. 8

iting cases are possible: (1) there is almost no dissociation in the liquid phase, hydration being complete; (2) the liquid is practically completely dissociated into $CaCl_2$ and H_2O. In the former case the lowering of the freezing point by the *first* additions of *either* $CaCl_2$ or H_2O to the liquid will be proportional to the number of mols added, and for a perfect solution would be expressed by equation (19) (p. 373). The two curves, one for additions of $CaCl_2$, the other for additions of water, would meet at nearly a sharp angle, and would be approximately straight lines for the first part of their course. Two such curves, *ab* and *ac*, are shown in Figure 8, which represents a melting-point curve

for a "pseudobinary" system, exhibiting a single compound between the two components.

In the second case, where the liquid is highly dissociated, it has been shown theoretically[47] and also experimentally[48] that the first additions of *either* of the products of dissociation, in this case $CaCl_2$ or H_2O, produce no effect upon the freezing point. The curve for this case will therefore be a single straight line or very flat curve, such as *bc* in Figure 8. These two curves represent the limiting cases between which all experimental curves will be found.

As regards hydration in the liquid phase, it can be definitely stated[49] that the mere existence of a solid crystalline hydrate in equilibrium with

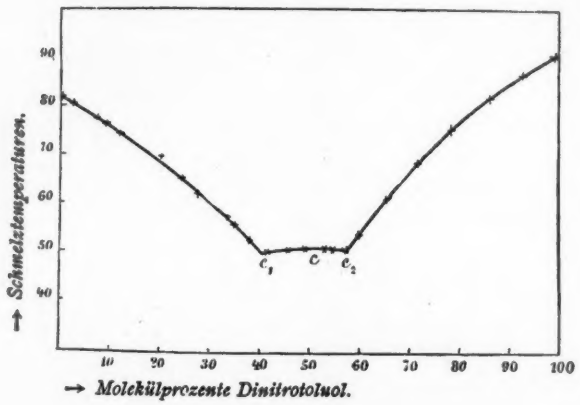

FIG. 9

its solution is proof of the existence of such a compound in the liquid phase; but whether the proportion of it is large or small is not thereby determined. The greater the dissociation in the fused state, the flatter will be the solubility curve at its vertex. The failure of a solid compound to exist in equilibrium with its solution is, however, no indication of the nonexistence of such compounds in the liquid phase. The heptahydrate of sodium sulphate is a familiar example of a crystalline hydrate which is not stable in contact with any aqueous solution of sodium sulphate

[47] Stortenbeker, Z. physik. Chem., 10, 183 (1892); Lewis, R. 6.

[48] Kremann, Monatshefte, 25, 1283 (1904).

[49] Roozeboom and Aten, Z. physik. Chem., 53, 465 (1905).

and whose solubility curve is only realized because of the slow transformation into the stable system. Many such instances are recorded, the most remarkable being the four crystalline hydrates of calcium chromate, none of which is stable in contact with any aqueous solution

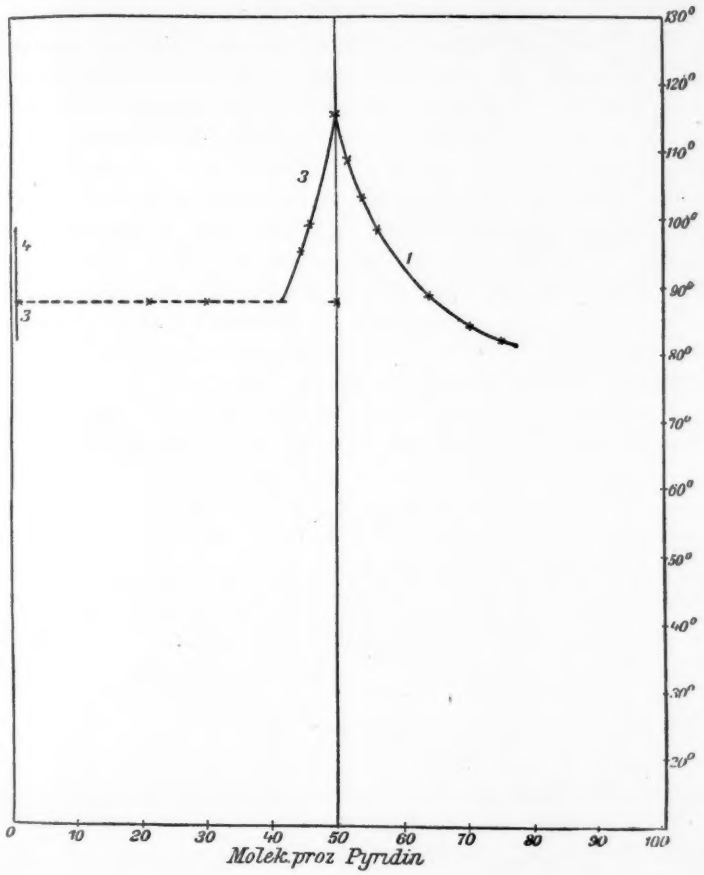

FIG. 10

of calcium chromate. That such hydrates exist in the solution, however, is shown by the fact that they can be precipitated by the addition of other substances, such as alcohol, to the solution.

Two examples taken from recent literature will serve to illustrate the two extreme types of solubility curves for compounds. In Figure 9

for the system dinitro-toluene-naphthalene (R. 48, p. 1283) we have an example of a high degree of dissociation in the liquid state. Figure 10 for the system methyliodide-pyridine[50] illustrates the other extreme, the compound showing little, if any, dissociation in the solution. The solubility curves of most hydrates show the same rounded summit as does $CaCl_2 \cdot 6H_2O$, and are therefore markedly dissociated in the liquid state. Attempts to compute the degree of dissociation from the shape of the solubility curve have been made in some cases.[51] Such calculations in the case of crystalline hydrates especially have little, if any, value, owing to the number of arbitrary assumptions which must be made. The most that can be said is that a rough idea of the dissociation in the liquid state can be obtained by an examination of the solubility curve of a crystalline hydrate.

In dealing with the solubility of one liquid in another, closed curves are obtained in certain cases, an upper and a lower critical temperature being observed. The case of nicotine and water studied by Hudson[52] will serve as an example. Above 210° and below 60° these two liquids are miscible in all proportions. The phenomenon of a closed solubility curve is held to be a characteristic of a ternary system. Thus Dologolenko has recently[53] shown that the closed curve previously obtained for the system water-secondary butyl alcohol is due to the presence of traces of tertiary butyl alcohol. When the perfectly pure secondary alcohol is employed, the lower critical temperature is not observed. In the case of the system nicotine-water, the closed curve, together with a considerable contraction and evolution of heat on mixing, led Hudson to the conclusion that a hydrate was formed in solution, thus making the system a "pseudoternary" one (to follow a nomenclature suggested by Roozeboom) and producing the typical closed curve of such a system. A similar closed curve has been recently obtained by Flaschner and MacEwen[54] for the system water-2-methylpiperidine.

B. Maximum Rate of Solution. — This method for studying the equilibrium between hydrate and anhydride in solution was developed

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[50] Aten, Z. physik. Chem., **54**, 127 (1905).

[51] Kremann, R. 48, also Sitzungsber. Wien Akad., **116**, 821 (1907); Findlay and Hickmans, J. Chem. Soc., **91**, 905 (1907); Van Laar, Kon. Akad. Weten., p. 711 (1906).

[52] Hudson, Z. physik. Chem., **47**, 113 (1904).

[53] Dologolenko, Z. physik. Chem., **62**, 499 (1908).

[54] Flaschner and MacEwen, J. Chem. Soc., **93**, 1000 (1908).

by C. S. Hudson[55] and applied by him to the study of the hydration of milk sugar in solution. Three forms of milk sugar are known, a hydrate, $C_{12}H_{22}O_{11}\cdot H_2O$, and two anhydrides, α and β, of which only the latter is involved in the following considerations.

When a large excess of the solid milk-sugar-hydrate is agitated with water, there is formed in a few minutes a solution whose concentration (called the initial solubility of the hydrate, S_o^H) is independent of the amount of the solid phase present. On continued agitation with water, however, the concentration of milk sugar in the solution increases slowly at a perfectly definite rate, called "the maximum rate of solution" (because it is not exceeded however much solid phase is present), until a final solubility, S_∞^H, is reached. This slow increase in solubility has been shown by Hudson to be due to a slow dehydration of a portion of the dissolved hydrate with the formation of a certain amount of the β anhydride in the solution.

The total increase in solubility, $S_\infty^H - S_o^H$, represents the concentration of β anhydride, which is in equilibrium with S_o^H mols of hydrate. Moreover, the rate of increase in the solubility, S^H, of the solid hydrate is equal to the rate of change of hydrate to anhydride in the solution, *i. e.*,

$$\frac{dS^H}{dt} = \frac{dC_A}{dt} = k_1 S_o^H - k_2 C_A, \tag{27}$$

where S^H is the concentration of the saturated solution at the time t, C_A (equal to $S^H - S_o^H$) is the concentration of the anhydride, and k_1, k_2 are the velocity constants of the two opposing reactions. On integration we obtain the equation,

$$\frac{1}{t} \ln \frac{S_\infty^H - S_o^H}{S_\infty^H - S^H} = k_2. \tag{28}$$

Measurements of the "maximum rate of solution" made at three different temperatures, 0°, 15°, and 25°, gave satisfactory values for k_2 in each case, and the values were found to be related to one another according to the usual equation,

$$\frac{d \ln k_2}{dT} = \frac{A}{T^2} \tag{29}$$

[55] J. Amer. Chem. Soc., **26**, 1065 (1904). See also a recent paper by Hudson and Brown, "The Heats of Solution of the Three Forms of Milk Sugar," *ibid.*, **30**, 960 (1908).

The separate velocity constants, k_1 and k_2, of the two opposing reactions of hydration and dehydration can be derived from solubility measurements, while from experiments on the rate of change of the optical rotation of freshly prepared milk sugar solutions their sum, $k_1 + k_2$, can be obtained. The two methods were found to give concordant results, so that the phenomenon of mutarotation in the case of milk sugar solutions certainly, and possibly in many other cases, is to be regarded as due to a slow change in the degree of hydration.[56]

The equilibrium constant of the hydration reaction in solution, as determined from the optical rotation, was found to be $\frac{C_A}{C_H} = K = 1.54$ at 20°, while the solubility experiments gave the value,

$$\frac{S^H - S^H_o}{S^H_o} = \frac{C_A}{C_H} = 1.48. \qquad (30)$$

By direct measurements of the equilibrium at different temperatures, and also by calorimetric determinations of the heat of the reaction, Hudson has shown conclusively that the hydration changes but little with the temperature, the change being, however, an *increase* in the degree of hydration with rising temperature. In this respect the reaction differs from most hydration reactions. This fact, together with the slow progress of the reaction at ordinary temperatures and the large change in optical rotatory power which accompanies it ($[a]^{20°}_D = 86.0$ for the hydrate and 35.4° for the anhydride), renders it probable that the hydration is not simply a union of water with the unhydrated molecule to form a loose complex, but that a rearrangement of the atoms within the milk sugar molecule takes place at the same time. The anhydride is the stable form above 94° (the transition point for hydrate and β anhydride). By using the solid β anhydride prepared by crystallization from the solution above 94°, Hudson was able to study the reverse reaction — the slow formation and precipitation of the hydrate at ordinary temperatures — and the results so obtained agreed satisfactorily with the corresponding ones for the direct reaction.

The Vapor Pressures and Freezing Points of Milk Sugar Solutions. — It may be interesting to compare the "average degree of hydration" of milk sugar in solution, as calculated from the variations from the

[56] With reference to other sugars, see the recent paper of Julius Meyer, Z. physik. Chem., 62, 59 (1908). Cf. also Roth's results on glucose, this review, p. 374.

laws of the "perfect solution," with the degree of hydration given by the "maximum rate of solution" method. Hudson[57] has determined the vapor pressures of saturated solutions of the milk sugar hydrate at temperatures ranging from 50° to 100°. For a saturated solution of milk sugar hydrate containing 2.29 mols of $C_{12}H_{22}O_{11}$ per 1,000 grams of water, Hudson found that $\Delta p = 10.8 \pm 0.4$ mm. Hg. The value of p for this temperature is 233.1, whence by substitution in equation (22) the value 3.6 ± 0.8 mols of water is obtained as the average molecular hydration which must be assumed in order to explain the deviation from the theoretical equation on the basis of hydration. Similarly, using Hudson's value, − 0.911°, for the freezing point of a milk sugar solution containing 0.4805 mol of $C_{12}H_{22}O_{11}$ per 1,000 grams of water and applying equation (19), the approximate value, 3 mols of water, is obtained as the average molecular hydration which must be assumed in order to explain the deviation from the theoretical value on the basis of hydration. If this explanation is correct, it requires that in addition to the peculiar and definite monohydrate of milk sugar and the β "anhydride" which exist together in these solutions there must be, also, more complex hydrates of a different character, corresponding more nearly to the usual type of hydrate, their formation not being attended by slowly progressing changes in the rotatory power of the molecule.

The method described in this section is restricted to substances which exhibit a maximum rate of solution, and is therefore not applicable to most electrolytes. Some results obtained by Roozeboom,[58] however, on the solubilities and transition points of the hydrates of thorium sulphate indicate strongly the possibility of the existence of a maximum rate of solution in this instance. He found that solubility measurements of $Th(SO_4)_2 \cdot 9H_2O$ could be made even at 55°, although the transition point of this hydrate into the tetrahydrate occurs at 43°. Similarly, from a saturated solution of the tetrahydrate at 20° the stable nonahydrate precipitated only very slowly even in contact with an excess of solid $Th(SO_4)_2 \cdot 9H_2O$, thus indicating that the change of tetrahydrate into nonahydrate in solution is a slow reaction. The study of the kinetics of this reaction should prove interesting.

C. Variations in the Distribution Ratio of a Solute between Two "Nonmiscible" Phases. — This method of studying complex formation

[57] Hudson, J. Amer. Chem. Soc., **30**, 1777 (1908).

[58] Roozeboom, Z. physik. Chem., **5**, 208 (1890).

between solvent and solute in solution has been applied by Hantzsch and Sebaldt[59] and by Hantzsch and Vagt.[60] It is based upon the assumption that the distribution of a solute between two nonmiscible solvents, or a solvent and a gaseous phase, is, at least approximately, independent of the temperature, the dilution, and the presence of a second dissolved substance; provided that the solute is a "normal solute," *i. e.*, one which exists in both phases as simple, unpolymerized molecules uncombined with either solute.

In order to appreciate the full significance of this assumption it will be analyzed more closely. When a substance is in distribution equilibrium between two phases, its activity must be the same in both phases, *i. e.*,

$$\xi_1 = \xi_2.$$

For the case that the substance forms a "perfect solution" in the two solvents (or acts also as a perfect gas in case one of the phases is gaseous) we have for a given temperature from equation (3),

$$\frac{N'_1}{1 - N'_1} = k \frac{N'_2}{1 - N'_2}.$$

As the solution becomes very dilute, this relation approaches the equation,

$$\frac{C_1}{C_2} = k,$$

which is Nernst's law for distribution between two solvents, also Henry's law for the solubility of a gas in a liquid.

The assumption that the quotient, k, is independent of the temperature requires that "normal" substances must in general have the same heat of solution in both solvents. Similarly, for the "normal" solute in the "normal" solvent the distribution law should not be affected by dilution or by the addition of a second "normal" solute.

For a series of substances of varied chemical character (*i. e.*, $HgCl_2$, HCN, $C_2H_4(CN)_2$, HCHO, $(CH_3)_2CO$, $CCl_3CH(OH)_2$), Hantzsch found that the distribution ratio between water and a second solvent, such as ether, benzene, chloroform, toluene, etc., was at least approximately constant over a considerable range of temperature. The following examples serve to illustrate this constancy. Concentrations are in mols per liter.

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[59] Hantzsch and Sebaldt, Z. physik. Chem., **30**, 258 (1899).

[60] Hantzsch and Vagt, *ibid.*, **38**, 705 (1901).

TABLE V

WATER ← CHLORALHYDRATE → ETHER

t.	C_w.	C_{Et}.	$k = \frac{C_w}{C_{Et}}$.
0°	0.178	0.764	0.233
10	0.178	0.764	0.233
20	0.180	0.766	0.235
30	0.180	0.766	0.236

TABLE VI

WATER ← MERCURIC CHLORIDE → TOLUENE, $t = 25°$

C_w.	C_{Tol}.	$k = \frac{C_w}{C_{Tol}}$.
0.2299	0.0201	11.4
0.1149	0.0101	11.4
0.0574	0.0051	11.3
0.0286	0.0026	11.0
0.0143	0.0013	11.0

TABLE VII

WATER ← ETHYLENE CYANIDE → CHLOROFORM, $t = 20°$

Addition.	C_w.	C_C.	$k = \frac{C_w}{C_C}$.
1 mol KOH	0.0790	0.0460	1.71
1 mol KCl	0.0788	0.0462	1.71
1 mol HCl	0.0791	0.0459	1.72

In contrast with these "normal" substances having constant distribution-coefficients, there exist a number of substances for which the distribution ratio varies greatly with the temperature. To this class belong the amines, ammonia, pyridine, bromine, iodine, and carbon dioxide. Variations in the distribution-coefficients are, however, even here, only marked in case one of the solvents is water or a liquid of similar type. Some examples of this type of substances are shown in the following tables. For an electrolyte the distribution law takes the form,

$$\frac{C_1(1-\gamma)}{C_2} = k,$$

where γ is the degree of dissociation in the aqueous solution.

TABLE VIII

WATER ← TRIMETHYLAMINE → TOLUENE

t.	C_w.	C_T.	100γ.	$k=\frac{C_w(1-\gamma_1)}{C_T}$.	$\frac{\Delta k}{\Delta t}$ per cent.
0°	0.0629	0.0084	3.31	7.2	. .
10	0.0582	0.0130	3.45	4.32	4.3
20	0.0535	0.0187	3.60	2.76	2.3
30	0.0477	0.0238	3.80	1.93	1.3
40	0.0417	0.0300	4.10	1.33	0.9
50	0.0360	0.0350	4.40	0.983	0.7
60	0.0322	0.0386	4.70	0.795	0.3
70	0.0270	0.0431	5.10	0.595	0.3
80	0.0233	0.0454	5.45	0.485	0.16
90	0.0225	0.0474	5.55	0.488	0.05
100	. .	. .	. .	[0.420 ext.]	. .

TABLE IX

WATER ← BROMINE → AIR

t.	C_w.	C_A.	$k=\frac{C_w}{C_A}$.	$\frac{\Delta k}{\Delta t}$ per cent.
0°	0.0245	0.00039	63.0	. .
10	0.0219	0.00056	39.0	4.3
20	0.0178	0.00077	23.0	2.8
40	0.0102	0.00095	10.7	0.8
60	0.0058	0.00096	6.0	0.3

TABLE X

WATER ← CARBONDIOXIDE → AIR

t.	C_w.	C_A.	$k=\frac{C_w}{C_A}$.	$\frac{\Delta k}{\Delta t}$ per cent.
0°	0.00805	0.00408	1.97	. .
10	0.00686	0.00496	1.38	4.0
20	0.00468	0.00427	1.11	1.9
40	0.00305	0.00416	0.74	0.8
90	0.00123	0.00327	0.38	0.3

The deviations from the behavior of the "normal" substance exhibited by this last class of substances are such as would result if the solute

in the water layer were hydrated to a greater or less degree. As the temperature is increased these hydrates break down gradually, so that the second solvent should extract more and more of the solute, since the equilibrium between the two layers is an equilibrium between the unhydrated molecules, and increase in temperature increases the proportion of unhydrated molecules in the water layer. This is illustrated by the figures in Tables VIII, IX, and X.[61]

The Physical Properties of Solutions in Relation to the Law of Mixtures

The physical properties of solutions which conform to the so-called law of mixtures are additive with respect to the constituents. This may be expressed mathematically by the equation,

$$X = x'N' + xN, \tag{31}$$

where X is the molecular property in question (*e.g.*, molecular heat, molecular volume, molecular refraction, etc.) and x' and x the corresponding molecular properties of pure solute and solvent, respectively, N' and N being, as before, the mol fractions of solute and solvent, respectively.

In cases where the law of mixtures is not obeyed it is customary to assume, provisionally, that the molecular property of the solvent remains unchanged and to ascribe all deviations from the law of mixtures to changes in the physical property of the solute. This procedure is found, however, in many cases to lead to absurd results for the molecular property of the solute in the solution. To explain these results, it has been assumed that complexes between solute and solvent are formed in the solution. In addition to these purely qualitative conclusions regarding the *existence* of such complexes, numerous attempts have been made to determine their formulæ by means of the positions of certain supposed discontinuities in property-composition curves. (The term property-composition curve will be applied to any curve expressing the change of some physical property of a solution with changes in its percentage composition.) Although the literature[62] contains a large number of

[61] See also Vaubel's [J. prak. Chem., **67**, 476 (1903)] measurements on the distribution of the aromatic phenols and amines between water and organic solvents.

[62] For a compilation of the literature on this portion of the subject, see Domke and Bein, Z. anorg. Chem., **43**, 125 (1905).

"compounds" of this character, only a few examples will be mentioned in the present discussion, since, probably without exception, the supposed points of discontinuity are due to experimental error. This statement applies even more strongly to compounds whose formulæ have been deduced from the position of supposed points of discontinuity in the first or second differential coefficient of a function connecting some physical property with composition.[63]

Although the existence of points of discontinuity in property-composition curves can be denied, striking irregularities sometimes occur. Some examples of these irregularities will be considered in what follows.

The following physical properties of solutions have, at different times and by various observers, been made the basis for conclusions regarding the existence of hydrates in solution: Heat-capacity, density, viscosity, refractivity, conductivity, compressibility, surface tension, coefficient of expansion, and heat of solution.

Heat-Capacity. — The molecular heat-capacity, C, of a solution whose components are both normal substances would be, according to the law of mixtures [equation (31)],

$$C = c'N' + cN. \tag{32}$$

Mixtures of carbon bisulphide and chloroform are examples of normal liquids which have been shown by Schüller[64] and by Winkelmann[65] to obey this law. Deviations from this law occur in both directions in water solutions. The heat-capacity of water-alcohol mixtures is always greater than that calculated from the law of mixtures, the maximum being reached in a solution containing about 20 per cent. of alcohol.[64]

In the case of most aqueous solutions, however, the heat-capacity of the solution is less than that calculated by the law of mixtures. For these solutions values for the molecular heat-capacity of the solute in the solution have been calculated under the assumption that the molecular heat of the solvent retains the same value which it possesses in the pure state. For most organic solutes the value thus obtained is found to be a constant, independent of the concentration. In the case of

[63] Pickering, J. Chem. Soc., **51** (1887); **57**, 64, 331 (1890). Lupton, Phil. Mag. [5], **31**, 418 (1891). Hayes, *ibid.*, **32**, 99 (1891). Rücker, *ibid.*, **32**, 304 (1892); **33**, 204 (1892). Pickering, *ibid.*, **32**, 90 (1892); **33**, 132, 426 (1892). Chem. News, **63**, 305 (1891); **64**, 1, 311 (1891). Ber. chem. Ges., **25**, 1104 (1892). In this connection see also a recent paper by Lowry, Science Progress, **3**, No. 9, 124 (1908).

[64] Schüller, Pogg. Erg., **5**, 116, 192 (1871).

[65] Winkelmann, Pogg. Ann., **150**, 592 (1873).

nearly all solutions of electrolytes, however, it has been shown by Thomsen [66] that the molecular heat-capacity of the solute in the solution is less than it is in the pure state and that it steadily decreases with dilution, finally passing through zero and becoming negative in dilute solutions.

Since a negative heat-capacity is without meaning, it is obvious that the heat-capacity either of the water as a whole, or a certain portion of it, is lowered by the presence of the solute. To account for this effect, Berthelot,[67] in 1879, assumed the presence of hydrates in the solution, the water in these compounds having a smaller heat-capacity than the uncombined water.

An extended treatment of the heat-capacities of aqueous solutions from this point of view has been recently made by Magie.[68]

Density and Expansion. — According to the law of mixtures the molecular volume, V, of a solution is expressed by the equation,

$$V = v'N' + vN. \qquad (33)$$

Numerous examples of substances obeying this law are found among organic compounds, chiefly the hydrocarbons and their substitution products.[69]

If the molecular volume of the solute in the solution be calculated under the assumption that the volume of the solvent is the same as it is in the pure state, it is found that in a few cases (*e.g.*, NH_4Cl, NH_4Br, $LiNO_3$) the value so obtained is greater than the volume of the pure solute. The process of solution in these cases is, therefore, attended by an expansion, the solution occupying a greater volume than the two constituents before mixing. In the vast majority of cases, however, the reverse is the case, the process of solution being accompanied by a contraction. On dilution of a concentrated solution this contraction continues, the molecular volume of the solute in the solution diminishing and approaching a constant value in dilute solution. In a number of cases it even becomes negative, so that the volume of the solution

[66] Thomsen, Thermochem. Unters., **1**, 53.

[67] See note 18, page 366, of this review.

[68] Magie, Proc. Amer. Phil. Soc., **46**, 138 (1907); Phys. Rev., **25**, 171 (1907).

[69] See a recent paper by Lumsden [J. Chem. Soc., **91**, 24 (1907)] in connection with this point.

is less than the original volume of the water used in preparing it.[70] This behavior and its close analogy to the corresponding behavior of

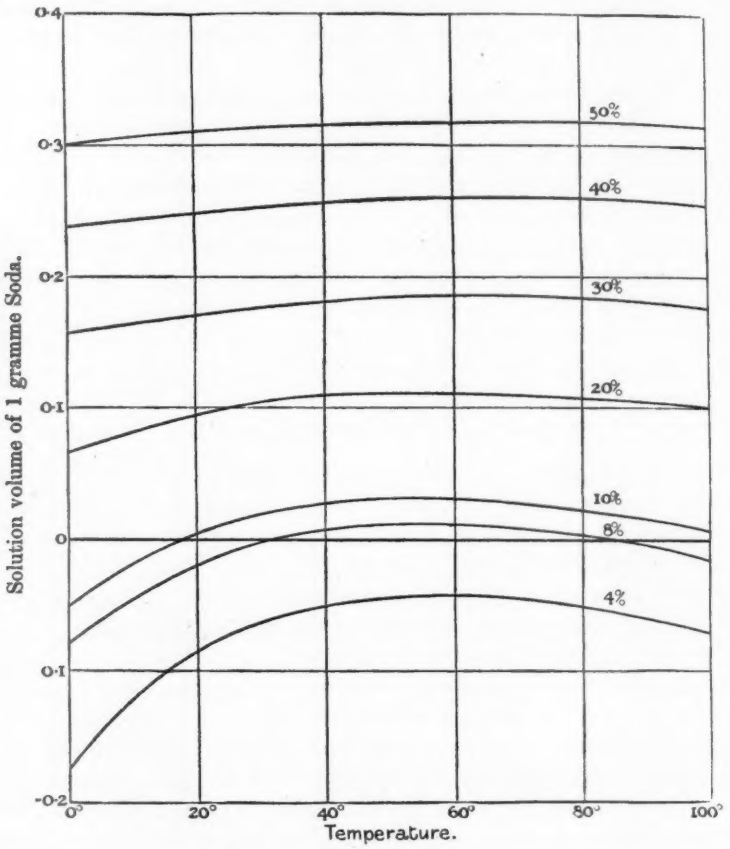

FIG. 11

the heat-capacities as described above were first pointed out by Julius Thomsen.[66]

[70] For example, sulphates of Cd, Co, Cu, Fe, Mg, Ni, and Zn [MacGregor, Trans. Roy. Soc., Canada, **8**, Sec. III, 19 (1890); also Pasea, *ibid.*, Sec. III, 27 (1900)]. Hydroxides of Na, Ba, Sr [Carse, Proc. Roy. Soc., Edinburgh, **25**, 281 (1904)]. LiOH, Na_2S, Na_2CO_3, NaH_2PO_4, and Na_2AsO_4 [Traube, Z. anorg. Chem., **3**, 25 (1893)]. NaOH [Bousfield and Lowry, Phil. Trans. A., **204**, 265 (1905)]. For recent tables of the molecular volumes of electrolytes in solution see Ruppin [Z. physik. Chem., **14**, 482 (1894)] and Forch [Ann. Phys., **12**, 591 (1903)].

A diagram illustrating the volume changes accompanying the dilution of sodium hydroxide solutions at different temperatures is shown in Figure 11, which is taken from the investigation by Bousfield and Lowry.[70] It will be noticed that the volume of the solute in the solution increases with rising temperature and eventually passes through zero and becomes positive for all except the most dilute solutions.

As early as 1872 attempts were made to find relations between the volume of water of crystallization and the density of salt solutions. Owing to insufficient and inaccurate data, these earlier investigators reached the conclusion that crystalline hydrates when dissolved in water dissociated completely into the anhydrous salt and water.[71]

In 1890 Schneider[72] made a careful study of the densities of solid crystalline hydrates and of their aqueous solutions at room temperature. He found that, on the assumption of a constant density for the anhydrous salt, the density of the water of crystallization in solid crystalline hydrates was about 1.2 for a large number of salts. Assuming, accordingly, that the water of crystallization remained attached to the salt when it was dissolved and retained the density 1.2, he calculated the density of the solution according to the law of mixtures and found much better agreement with the observed value than was obtained when this correction was not made. Traube,[73] in 1893, extended these calculations to a larger number of compounds and arrived at the same conclusions, namely, that the density data indicate that salts are hydrated in aqueous solution.

The argument involved here is obviously of the same nature as that used in the heat-capacity method. A negative volume for the solute in solution being impossible, a portion of the solvent, at least, must be denser than the pure solvent. To account for this increase in density it is assumed that a portion of the solvent is combined with the solute, thereby becoming compressed, the assumption being borne out by the increased density of water of crystallization in solid crystalline hydrates.

Turning now to examples of cases where density curves have been used to determine the formulæ of hydrates in solution, we will consider

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[71] Favre and Valson [Compt. rend., **75**, 334 (1872); **79**, 968, 1037 (1874)]. Southworth [Amer. Jour. Sci., **117**, 399 (1879)]. Nichol [Phil. Mag., **16**, 121 (1883), **18**, 179 (1884); Chem. News, **54**, 191 (1886)]. Wanklyn, *et al* [Chem. News, **64**, 27, 39, 51, 146 (1891); Phil. Mag., **32**, 473 (1891)].

[72] Schneider, Sitzungsber. d. k. Akad. Wien, **99**, May (1890); Monatshefte, **11**, 166 (1890).

[73] Z. anorg. Chem., **3**, 24 (1893).

the solutions of sulphuric and of nitric acids. Owing to the recent investigations of Domke and Bein,[74] of Veley and Manley,[75] of Küster and Kremann,[76] and of Kremann and Ehrlich,[77] we are in possession of considerable data on the physical properties of these solutions.

We will consider first the melting-point diagrams of the two systems in order to find what solid hydrates are known and what is the range of stability of each of them. The diagram (R. 76, p. 22) for the system

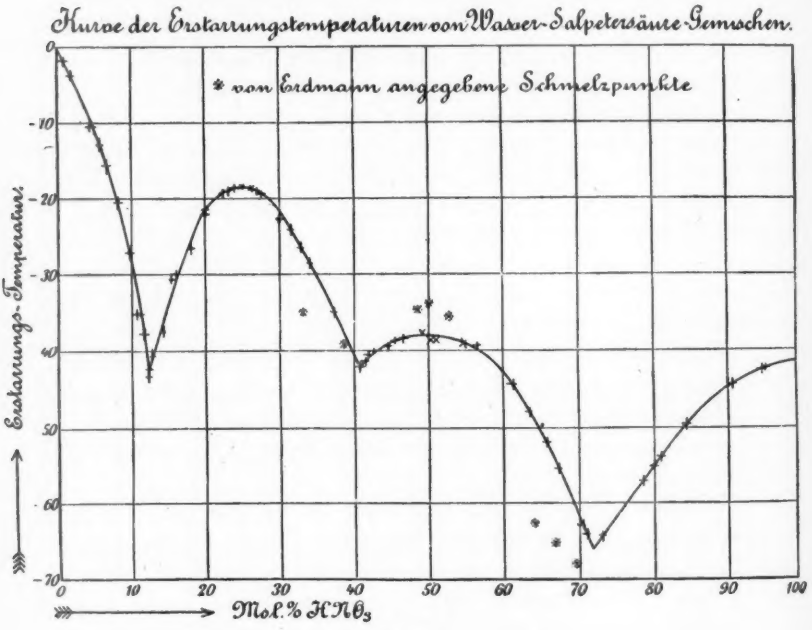

FIG. 12

$HNO_3 - H_2O$ (Fig. 12) shows the existence of two solid hydrates, $HNO_3 \cdot 3H_2O$ and $HNO_3 \cdot H_2O$. Judging from the shapes of the summits of their solubility curves the monohydrate is more dissociated in

[74] Domke and Bein, Wiss. Abhandl. Eich. Komm., **5**, 257 (1904).

[75] Veley and Manley, Proc. Roy. Soc., London, **69**, 96 (1901).

[76] Küster and Kremann, Z. anorg. Chem., **41**, 33 (1904).

[77] Kremann and Ehrlich, Sitz. Wein Akad., **116**, 733 (1907).

solution than the trihydrate. The melting-point diagram[78] for the system $SO_3 - H_2O$ (Fig. 13) shows the existence of three solid hydrates of sulphuric acid, viz., $H_2SO_4 \cdot H_2O$, $H_2SO_4 \cdot 2H_2O$, and $H_2SO_4 \cdot 4H_2O$, only the first one being capable of existence above $-15°$, however.

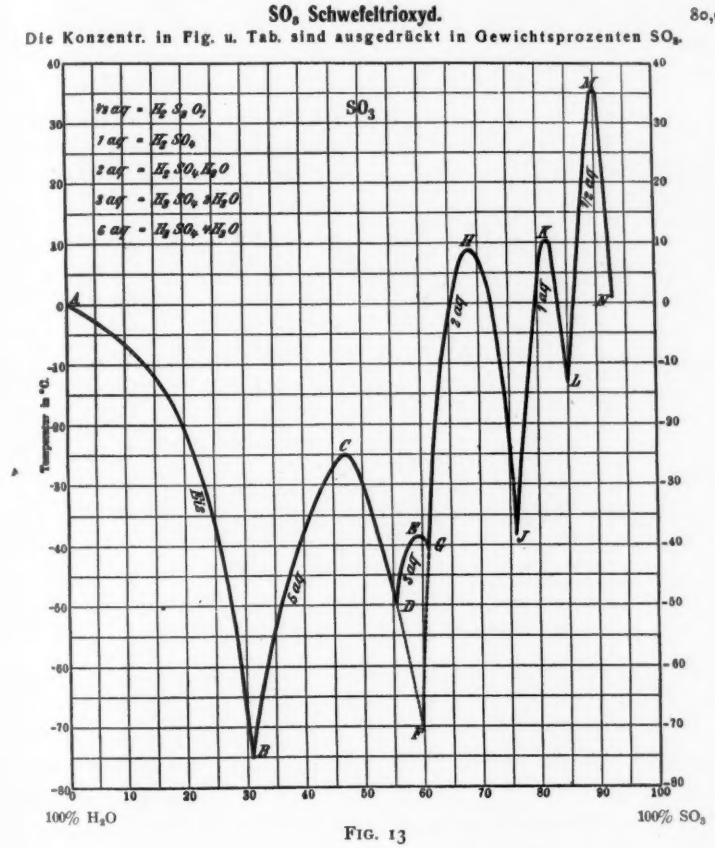

FIG. 13

In the curve showing the relation between the density and composition of nitric acid solutions, Veley and Manley (R. 75, p. 119) found that points of discontinuity occurred at "points corresponding to the

[78] This diagram, prepared by Meyerhoffer from all existing data, is on page 567 of the last edition of Landolt and Börnstein.

composition of hydrates of HNO_3 with 14, 7, 4, 3, 1.5, and 1 molecule of water, respectively."

These points of discontinuity must, however, be regarded as due to experimental errors. Domke and Bein, in their exhaustive investigation of sulphuric acid solutions, have shown most clearly and conclusively that breaks of this kind do not occur in density curves and that no reliable results concerning the formulæ of hydrates can be drawn from density curves. The matter is aptly stated by Küster and Kremann (R. 76, p. 31) as follows: "Ein beliebtes und deshalb häufig, aber meist ohne die erforderliche Kritik angewendetes Verfahren, 'Hydrate' in Lösungen verdünnter Sauren nachzuweisen ist die Ermittelung der

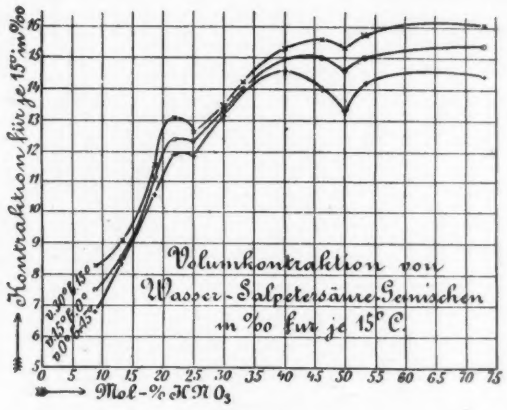

FIG. 14

Volumgewichte, 'Knicke,' and zwar in der Regel mit grosser Kunst and gelinder Gewalt in den Volumgewichtskurven aufgefundene 'Knicke,' zeigen dann so viel 'Hydrate' an, als der Geduld des Experimentators entsprechen. Diese Methode ist auch von Veley schon vor einigen Jahren mit bestem Erfolg bei der Salpetersaure angewendet worden."

These investigators accordingly studied the expansion coefficients of nitric acid solutions and discovered irregularities in the neighborhood of compositions corresponding to the hydrates $HNO_3 \cdot H_2O$ and $HNO_3 \cdot 3H_2O$, which they attributed to the presence of these compounds in the solution. Their results are shown in Figure 14. Contractions (expressed in parts per thousand) for temperature changes of 15° at different intervals are plotted as ordinates and mol per cent. of HNO_3 as abscissæ.

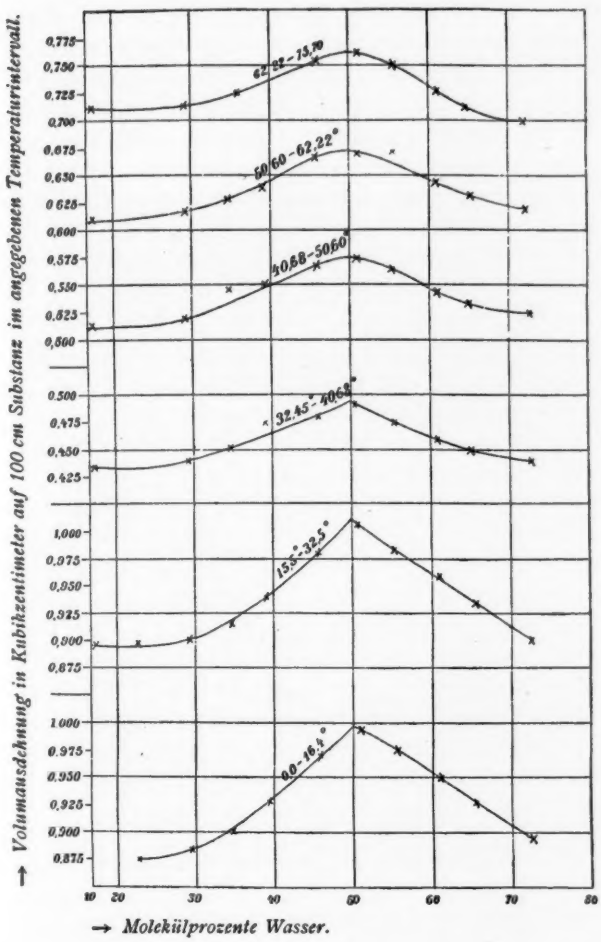

FIG. 15

A similar set of curves[79] for the system $H_2SO_4 - H_2O$ is shown in Figure 15. The curves at the lower temperatures show an irregularity[80] in the neighborhood of the composition corresponding to the hydrate

[79] From Kremann and Ehrlich, R. 77, p. 749.

[80] None of these irregularities should be represented as points as they are shown in these figures and also in Figure 17, since abrupt changes cannot occur in such curves. The irregularities represent only maxima and minima.

$H_2SO_4 \cdot H_2O$. No irregularities appear, however, in the neighborhood of compositions corresponding to the di- and tetra-hydrates, whose solubility curves are shown in Figure 13. The irregularity is seen to become less and less distinct as the temperature rises, which the authors attribute to the gradual dissociation of the monohydrate into its constituents. For the system aniline-nitrobenzene, which do not form any compound with each other, these investigators showed the absence of any such irregularities and of any decided temperature effect.

Viscosity. — According to Dunstan[81] the viscosity curves of mixtures fall into three classes: (1) Curves which obey the law of mixtures; (2) curves displaying minima; (3) curves displaying maxima. In case of curves displaying minima, according to Dunstan, the process of solution is accompanied by a decomposition of associated into simple molecules. The presence of maxima is attributed to the formation of complexes between the constituents. Numerous examples of each type will be found in the papers of Dunstan and his co-workers, also in recent papers by Tsakalotos,[82] Getman,[83] Kremann and Ehrlich,[77] and Beck and Ebbinghaus.[84]

As in the case of the density curves, we find mentioned in the literature numerous hydrates whose formulæ have been deduced from the positions of certain supposed points of discontinuity in viscosity curves belonging to the third type. Thus for the system $CH_3OH - H_2O$ we have, according to Varenne and Godefroy,[85] hydrates containing 1, 2, 3, 5, 8, and 20 molecules of water, respectively, but according to Dunstan[86] only the di- and tri-hydrates. Similarly, four hydrates of acetone[87] and seven of ethyl alcohol[88] have been announced recently, based upon the same evidence.

That these points of discontinuity in the viscosity curves of methyl-

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[81] Dunstan, Z. physik. Chem., **49**, 590 (1904); **51**, 732 (1905); **56**, 370 (1906). Trans. Chem. Soc., **85**, 817 (1904); **91**, 83 (1907).

[82] Tsakalotos, Bull. Soc. Chim. (4), **3**, 224, 242 (1908).

[83] Getman, J. Chim. Phys., **4**, 386 (1906).

[84] Beck and Ebbinghaus, Z. physik. Chem., **58**, 436 (1907).

[85] Varenne and Godefroy, Compt. rend., **138**, 990 (1904).

[86] Dunstan, Z. physik. Chem., **49**, 595 (1903).

[87] Varenne and Godefroy, R. 85, p. 992.

[88] Varenne and Godefroy, Compt. rend., **137**, 993 (1903); Dunstan, R. 86, p. 593; Gaillard, J. chim. Pharm., **6–26**, 481 (1907).

alcohol-water mixtures are purely imaginary and due to experimental errors will be evident from an examination of Figure 16, which contains Getman's viscosity curves (R. 83, p. 391) for this system at a

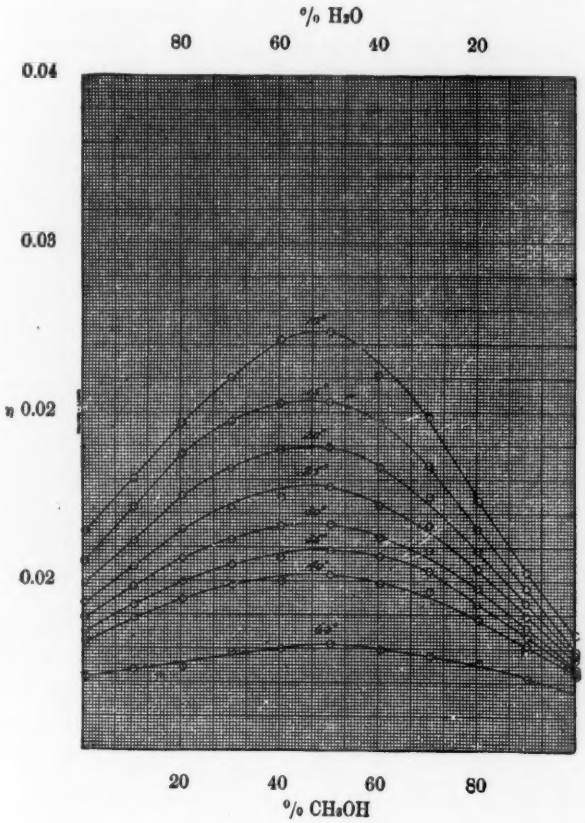

FIG. 16

series of temperatures. The absence of any points of discontinuity is immediately evident.

Kremann and Ehrlich also made viscosity measurements on mixtures of sulphuric acid and water at a series of temperatures. Their results are shown graphically in Figure 17. The curve for 0° shows a maximum (but not a point, as drawn in the figure) somewhere between

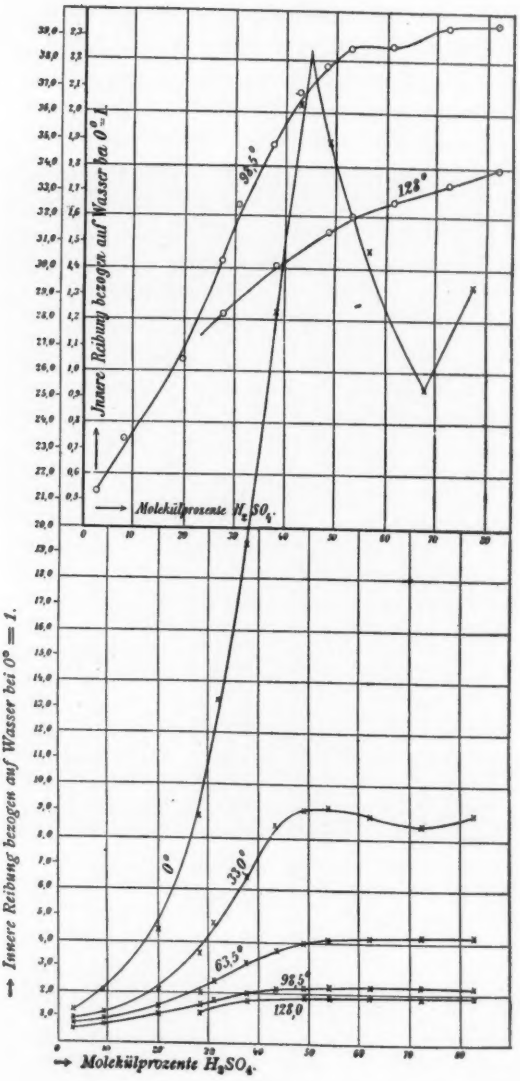
Innere Reibung bezogen auf Wasser bei 0° = 1.
Molekülprozente H_2SO_4.
98,5°
128°
0°
33,0°
63,5°
98,5°
128,0
Innere Reibung bezogen auf Wasser bei 0° = 1.
Molekülprozente H_2SO_4.

FIG. 17

40 and 50 mol per cent. and a minimum in the neighborhood of 70 mol per cent.[89] With rising temperature these irregularities become less and less marked, finally disappearing. The authors regard the position of the maximum as further evidence of the existence of the compound $H_2SO_4 \cdot H_2O$ in the solution.

Other Physical Properties. — The law of mixtures, applied to such properties as compressibility, surface tension, refractivity, magnetic rotation of the plane of polarization, etc., has been used but seldom in attacking the problem of complex formation in solution. The principles involved are quite similar to those discussed in the preceding sections, and it is not therefore necessary to treat them individually.[90]

Heat of Solution. — The law of mixtures requires that mixing of two normal liquids shall take place without absorption or evolution of heat. In cases where the process of solution consists to a large extent of a union between solvent and solute to form one or more hydrates in solution, a parallelism between heat of solution and degree of hydration in certain cases might be expected. Such a parallelism is found when the heats of solution of salts with a common anion are compared with other properties depending upon hydration, such as freezing-point and vapor-pressure lowering.[91] This parallelism is evident in the accompanying table[92] (Table XI), which contains the heats of solution (in joules) of a number of salts. Compare this review, page 364.

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[89] Cf. Dunstan and Wilson, Trans. Chem. Soc., **91**, 85 (1907).

[90] References: Veley and Manley, R. 75, p. 118. Röntgen and Schneider, Wied. Ann., **29**, 196, 208 (1886). Whatmough, Z. physik. Chem., **39**, 129 (1901). Knietsch, Ber. deutsch. Chem. Ges., **34**, 4110 (1901). Linebarger, J. Amer. Chem. Soc., **22**, 5 (1900). Ramsay and Ashton, J. Chem. Soc., **65**, 167 (1899). Grünmach, Abhandl. Eich. Komm., **3**, 174 (1902). Volkmann, Wied. Ann., **11**, 194 (1880); **17**, 368 (1882). Quincke, Pogg. Ann., **160**, 347 (1877). Kremann and Ehrlich, Sitzungsber. Wien Akad., **116**, 740 (1907). Bousfield, Phil. Trans., **206**, 150 (1906). Getman and Wilson, Amer. Chem. J., **40**, 468 (1908).

[91] As shown by Tammann, Mem. Acad. Sci., St. Petersburg (7), **35** (1887).

[92] From the paper of Biltz, R. 15, p. 211.

TABLE XI

HEATS OF SOLUTION IN JOULES

ALKALI GROUP

	NO_3.	SCN.	CN.	Cl.	Br.	I.
K	−36	−25	−12.6	−13	−21	−21
NH_4	−26	. .	. .	−17	−1	−15
Na	−21	. .	. .	−5	−1	+5
Li	+1	. .	. .	+35	. .	. .

ALKALINE EARTH GROUP

	Cl_2.	Br_2.
Ba	+9	+21
Sr	+46	+67
Ca	+73	+102
Mg	+100	. .

The heat of solution of a solid salt is doubtless a composite quantity, including, as it does, the heats of disgregation, of ionization, etc., as well as heat of hydration, so that a parallelism is the most that could be expected. Heat of dilution of a concentrated solution would probably be a better basis for comparison if sufficient data were available.

The parallelism shown in Table XI between the heat of solution of the various salts and their effects upon the lowering of the freezing points is, nevertheless, very striking. In the case of the alkali salts, for example, the heat due to hydration apparently increases with decrease in atomic weight, becoming finally, in the case of lithium salts, sufficiently great to more than compensate for the negative heat of disgregation of the solid salt.

An extended discussion of the thermochemistry of aqueous solutions of electrolytes will be found in a paper by Bousfield and Lowry.[98]

Final Conclusions Regarding the Methods Depending upon Physical Properties. — In the general tendency of many investigators to attribute the peculiarities of the physical properties of concentrated aqueous solutions to the presence of hydrates, certain important relations brought

[98] "The Thermochemistry of Electrolytes in Relation to the Hydrate Theory of Ionization," Trans. Far. Soc., **3**, 123 (1907).

out by Tammann[94] do not seem to have received the consideration which they deserve. Tammann has shown that, as regards many of its physical properties, a salt solution resembles the pure solvent under an increased external pressure Thus, for example, the phenomena which we have mentioned regarding the effects of salts upon the heat-capacity, viscosity, coefficient of expansion, etc., of the solvent can all be reproduced by simply subjecting the pure solvent to an increased external pressure.

There is considerable evidence to support the conclusion that water is a highly associated liquid, especially at low temperatures, and that the breaking down of the complex water molecules into simpler ones, such as occurs, for example, when the temperature is raised, is attended by a decrease in volume.[95] If this is the case, the effect of increasing the external pressure would be to cause a dissociation of complex molecules into simpler ones. The effect of pressure in decreasing the specific heat, specific volume, viscosity, etc., is more marked at lower temperatures, which is likewise the case for the effects of salts upon these properties.

These facts render it highly probable that a large part of the abnormal effects of salts upon the physical properties of water should also be ascribed to changes in the complexity of the solvent.[96] It may, indeed, be true that hydration is the mechanism by which these changes are brought about; but such a conclusion, drawn from the study of physical properties alone, must be regarded as highly speculative.

We are therefore forced to conclude, in spite of the extensive literature on this phase of the subject, that methods of studying hydration which depend upon the deviations of any physical property of a solution from the law of mixtures are incapable of yielding any *conclusive* information regarding the complexity or even the existence of hydrates in aqueous solution.

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[94] "Über die Beziehungen zwischen den inneren Kraften und Eigenschaften der Lösungen." Hamburg and Leipzig (1907).

[95] Sutherland has treated this subject extensively in a series of papers in the Philosophical Magazine, *q. v.* [6], **14**, 1 (1907), and [5], **50**, 460 (1900). See also Röntgen, Wied. Ann., **45**, 91 (1891), and Stradling, J. Frank. Inst., **152**, 257 (1901).

[96] This hypothesis, in various forms, has been advanced by numerous writers on the subject of aqueous solutions in recent years.

SECTION II. METHODS DEPENDING UPON DIFFUSION COEFFICIENTS AND IONIC MOBILITIES

Introduction

In this group are included those methods of studying hydration which depend upon kinetic or mechanical theories regarding certain properties of solutions and phenomena occurring in them. These methods have, up to the present time, been almost entirely confined to solutions of electrolytes, only a single instance of an application to a nonelectrolyte having come to my notice. This section of the review will therefore deal chiefly with that portion of the Ionic Theory which treats from a kinetic standpoint such phenomena as (1) ionic conductivities and diffusion coefficients, and the effects of changes of temperature, of concentration, and of the nature of the solvent upon these quantities; (2) the relation between the size of the ions and certain physical properties of the solution, such as density, viscosity, etc.; (3) transference effects accompanying electrolysis.

Owing to the nature of the methods included in this and the following section (which in some cases are based upon hypotheses which have not yet received general acceptance), I have endeavored, as far as practicable, to present the different theories in the words of the individual investigators.

The Hydration of Cane Sugar in Solution from the Standpoint of the Kinetic Theory

From purely kinetic considerations, Einstein[97] has recently derived the following expression connecting the viscosity coefficient, k, of a dilute solution with that, k_o, of the pure solvent, and with the volume, v, occupied by the solute molecules per unit volume of solution,

$$\frac{k}{k_o} = 1 + v.$$

In the derivation of this equation it is assumed that the solute molecules are spheres which are large in comparison with the molecules of the

[97] Einstein, "Eine neue Bestimmung der Molekül-Dimensionen," Ann. Phys. [4], 19, 301 (1906).

solvent among which they move. The author applied the formula to the data for a 1 per cent. sugar solution, and found that the presence of the sugar produced a greater effect upon the viscosity of the medium than was to be expected from the kinetic theory. He states his conclusions as follows (R. 97, p. 301): "Während also die Zuckerlösung, was ihre Dichte anbelangt, sich wie eine Mischung von Wasser und festem Zucker verhält, ist der Einfluss auf die innere Reibung viermal grösser, als er aus der Suspendierung der gleichen Zuckermenge resultieren würde. Es scheint mir dies Resultat im Sinne der Molekulartheorie kaum anders gedeutet werden zu können, als indem man annimmt, dass das in Lösung befindliche Zuckermolekül die Beweglichkeit des unmittelbar angrenzenden Wassers hemme, so das ein Quantum Wasser, dessen Volumen ungefähr das Dreifache des Volums des Zuckermoleküls ist, an das Zuckermolekül gekettet ist."

This conclusion is thus in qualitative agreement with the results of the methods discussed in Section I.

Comparative Ionic Hydration as Indicated by Ionic Conductances

The remarkable fact early attracted attention that, in the case of the ions of elements belonging to any one group of the periodic system, those of the elements of smaller atomic weights and smaller atomic volumes possess a lower equivalent conductance and therefore a smaller migration-velocity. A striking example of this is offered in the case of the alkali metals, as shown by the following table (Table XII), in which Column II contains the atomic weight of the element, Column III its atomic volume in the solid state, and Column IV the equivalent conductance of its ion at 18° as derived by Kohlrausch.

TABLE XII

I.	II.	III.	IV.	V.
	At. wt.	At. vol.	$l_{18°}$.	$k \cdot 10^7$.
Li	7.0	13.1	33.4	7.6
Na	23.0	23.7	43.5	7.4
K	39.1	45.5	64.6	6.0
Rb	85.5	56.0	67.5	5.3
Cs	132.9	7.1	68.0	5.2

This anomalous behavior is also shown by the viscosity coefficients of the ions, the ions of the larger and heavier atoms having the smallest viscosities.[98] As a possible explanation of this anomaly, Bredig[99] suggested that the lighter ion might have a larger cross-section or be so shaped as to offer a larger resistance. If such were the case, the rates of diffusion of these metals in mercury might be expected to show a similar behavior. This is not the case, however, as is shown by Column V of the above table, which contains the diffusion coefficients (k) of the alkali metals in mercury. The rates of diffusion are in the same order as would be expected from the atomic weights and atomic volumes of these elements.[100] To explain this apparent anomaly it has been assumed[98,99] that the ions are hydrated, those of the lighter elements in a given group being more hydrated (and therefore really larger and heavier) than those of the heavier elements. By referring again to Table XII and to page 364, Section I, of this review, it will be noticed that this assumption places the alkali elements in the same order as regards their relative degrees of hydration as was deduced from the relative effects of their salts upon the activity of the solvent. A direct proof of the correctness of this explanation, as well as a determination of the relative amounts of water in combination with some of these ions, has been described in a preceding communication (R. 120*a*).

Ionic Conductances as Affected by Changes in the Temperature and Viscosity of the Medium

More than a quarter of a century ago, and five years before the announcement of the Theory of Electrolytic Dissociation by Arrhenius, Stephan[101] studied the relation between the fluidity and the electrical conductivity of dilute solutions of electrolytes, and came to the conclusion that the ions were hydrated and carried a portion of the solvent with them as they moved through the solution; the evidence which led him to this conclusion being very similar to that which, twenty years later, caused Kohlrausch to propose a similar hypothesis as an

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[98] Euler, Wied. Ann., **63**, 273 (1897).

[99] Bredig, Z. physik. Chem., **13**, 277, N. 2 (1894).

[100] These diffusion coefficients are from an investigation by von Wogau, Ann. Phys., **23**, 369 (1907). Euler has shown (R. 98) that a similar relation holds true for the diffusion coefficients of the halogens in non-aqueous solvents.

[101] Stephan, Wied. Ann., **17**, 673 (1882).

explanation of the striking relationships between the values of the ionic conductances and their temperature coefficients. Stephan determined the fluidities and electrical conductivities of dilute solutions of the chlorides and iodides of the alkali metals in mixtures of alcohol and water of varying composition. He found that at constant temperature, but with varying amounts of alcohol, the conductances, Λ_∞, of very dilute solutions of these salts and the viscosities, η, of the medium obeyed the law,

$$\Lambda_\infty \eta = \text{const.}, \qquad (34)$$

for mixtures all the way from pure water up to the mixture of maximum viscosity containing 50 per cent. of alcohol. This range includes a threefold increase in the viscosity, η, of the medium. As a further support of his conclusions he pointed out that the temperature coefficients of the conductances in the different mixtures and also in pure water were almost identical in every case with the temperature coefficients of the viscosity of the medium. These results pointed to the conclusion (R. 101, p. 700), "dass jedes Ionenmolecul die benachbarten Molecule des Lösungsmittels einfach mitnimmt."

Our knowledge regarding the conductivities and viscosities of solutions of electrolytes in mixed solvents has been greatly enlarged by the recent experiments of Jones and his co-workers.[102] Their experiments demonstrate clearly that in all cases a marked parallelism exists between the conductivity and the fluidity of the solvent. A minimum in conductivity is always accompanied by a minimum in fluidity, both occurring at approximately the same percentage composition. Further discussion of conductivity in mixed solvents would necessarily involve a consideration of the problem of solvation in general, which would lead us beyond the bounds of this review. The phenomenon of hydration in solution is only one part of the general problem of solvation in solution. It is not the purpose of the reviewer to discuss this problem in other solvents than water, however, and the reader interested in this phase of the subject should consult the excellent review by Carrara[103] of "The Electro-Chemistry of Non-aqueous Solutions."

[102] Jones *et al.*, "Conductivity and Viscosity in Mixed Solvents," Carnegie Inst. Pub. No. 80 (1907). See also a recent investigation by Hartley, Thomas, and Applebey [Trans. Chem. Soc., **93**, 538 (1908)]. These investigators studied solutions in mixtures of water and pyridine. They found that the $\Lambda_\infty \eta$ product decreased regularly with increase in pyridine content until the solvent contained 67 per cent. of pyridine. Compare also a recent paper by Pissarjewski and Karp [Z. physik. Chem., **63**, 257 (1908)] on the relation between the diffusion coefficient, the viscosity, and the electrical conductivity of solutions.

[103] Carrara, Gaz. Chim. Ital., **37**, I, 525 (1907); also Ahrens Sammlung, **12**, 404 (1908).

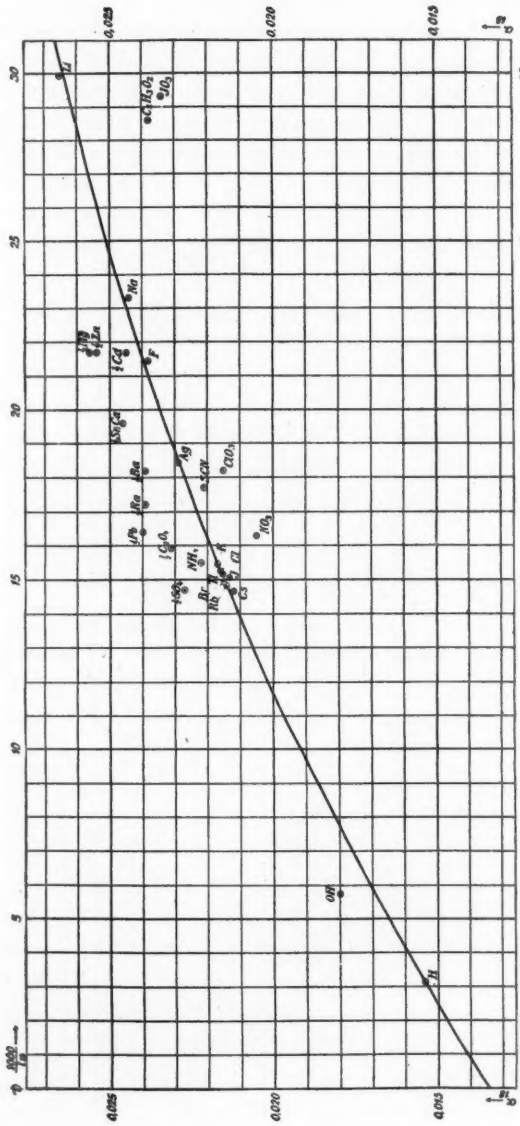
0.025
0.020
0.015
30
25
20
15
10
5
0
Li
$C_2H_3O_2$
ClO_3
Na
Zn
Cd
F
$SrCl_2$
Ag
SCN
ClO_3
NO_3
Cs
OH
H

FIG. 18

The Hypothesis of Kohlrausch. — Fr. Kohlrausch has expressed the opinion [104] that the relationships existing between the values of the ionic conductances and their temperature coefficients are such that it is scarcely possible to understand them except on the hypothesis that "about every ion moves an atmosphere of the solvent, whose dimensions are determined by the individual characteristics of the ion," and that "the electrolytic resistance of an ion is a frictional resistance that increases with the dimensions of the atmosphere." One of the most important relationships which led Kohlrausch to this conclusion is the fact that the temperature coefficient, α, for the conductance, l, of a given ion is a function of the conductance itself, and can be expressed by the equation,

$$\alpha = a + b\left(\frac{1}{l_{18°}}\right) + c\left(\frac{1}{l_{18°}}\right)^2, \qquad (35)$$

where $a = 0.01341$, $b = 0.640$, and $c = 6.94$. The graph of this equation, together with the loci of the values of l for numerous ions, is shown in Figure 18.[105] The further presentation and discussion of the relations derived by Kohlrausch are presented in his own words (R. 105, p. 130): "Aus dem ganzen Temperaturverhalten muss man den Schluss ziehen, dass der Ionenwiderstand wesentlich bedingt ist durch Wasserhüllen, die dem Ion, je nach seiner Individualität in verschiedener Grösse, anhaften, d. h. mit ihm wandern. Dass ein, in einer Flüssigkeit enthaltenes Atom oder ein Atomkomplex daselbst nicht wandern kann, ohne Teile des Lösungsmittels mit zu ziehen, wenn das wandernde obendrein, so wie hier, elektrisch geladen ist, muss man von vornherein annehmen.

. . . "Macht man die Annahme, dass der elektrolytische Widerstand eines Ions wesentlich in dem molekularen Reibungswiderstand seiner Wasserhülle besteht, also um so grösser ist, je mehr Wasserteile mitwandern, so wird nun eine Reihe von Erscheinungen begreiflich, die sonst unvermittelt dastehen.

. . . "Die Temperatur wirkt auf den elektrolytischen Widerstand mit derselben Grössenordnung ein, wie auf die Viskosität des Wassers, und zwar nähern sich in dieser Hinsicht die wenigst beweglichen, *i. e.*, die durch eine dicke Wasserhülle ihrer Individualität am meisten entkleideten Ionen dem Temperaturkoeffizienten der Wasserreibung.

[104] Kohlrausch, "The Resistance of the Ions and the Mechanical Friction of the Solvent," Proc. Roy. Soc., London, **71**, 338 (1903).

[105] See Kohlrausch, Z. Electrochem., **14**, 130 (1908).

"Weiter konvergieren die Formeln, welche die Temperaturabhängigkeit in weiteren Grenzen darstellen, nach unten verfolgt, nach ungefähr demselben Nullpunkt der Leitfähigkeit; zu nahe dem gleichen Nullpunkt für die Fluidität des Wassers führt auch die Temperaturformel der Wasserreibung."

The curves showing this extrapolation are given in Figure 19.[104] The fluidity of water when calculated in the same way as the conductivity, with the quadratic formula, is represented by the lowest curve. The extrapolated portions of all these curves pass through zero between $-35°$ and $-41°$.[106]

"Verstärkt werden diese Argumente dadurch, dass, wie ich vor 30 Jahren gezeigt habe, der elektrolytische Widerstand der Ionen, in mechanischen Einheiten gemessen, von derselben Grössenordnung ist, wie der mechanische Widerstand der Wassermoleküle, wenn man diesen aus der Reibungskonstante des Wassers und der, aus anderen Erscheinungen abgeleiteten Grösse der Moleküle berechnet.

"Endlich ist ja aber auch der Gegenstand dieses Aufsatzes, nämlich die Tatsache, dass die Beweglichkeit und ihr Temperaturkoeffizient bei so mannigfaltigen Körpern, wie Alkalimentalle, Fluor, Silber, Chlor, Thallium, durch ein und dasselbe Gesetz aneinander geknüpft sind, ohne eine Vermittelung fast widersinnig. Es muss offenbar etwas da sein, was die grundverschiedene Einzelnatur dieser Ionen aus dem Zusammenhange eliminiert hat. Dieses dritte, allen Vorgangen Gemeinsame kann man nur im Lösungsmittel suchen, und in der Tat, durch die Annahme, dass der Ionenwiderstand nicht die direkte Aeusserung einer Eigenschaft des Ions ist, sondern dass die direkte Wirkung des letzteren nur im Binden ungleicher Wasserhüllen besteht, wird der gesetzmässige Zusammenhang zwischen der Grösse der Beweglichkeit und der Grösse ihres Temperaturkoeffizienten, wenn auch vorerst noch nicht ins einzelne verfolgbar, doch wenigstens durchsichtig. Man ist nicht mehr verwundert, wenn der Temperatureinfluss auf Ionen von grossem Widerstand, d. h. von dicken Wasserhüllen, sich dem Einfluss auf die Reibung des Wassers selbst nähert. Dass der Temperatureinfluss auf die beweglicheren Ionen nicht genau derselbe ist, haben wir irgend einer Art von Mitwirkung des Ionenkernes zuzuschreiben, sei es einer direkten auf die Reibung im Lösungsmittel oder einer Wirkung,

[106] See also W. Hechler, "Fluidität und Leitfähigkeit einigen konzentrierter Salzlösungen unter 0°," Ann. Phys., [4], 15, 157 (1904); also R. Hosking, "Electrical Conductivity and Fluidity," Phil. Mag., [6], 7, 469 (1904).

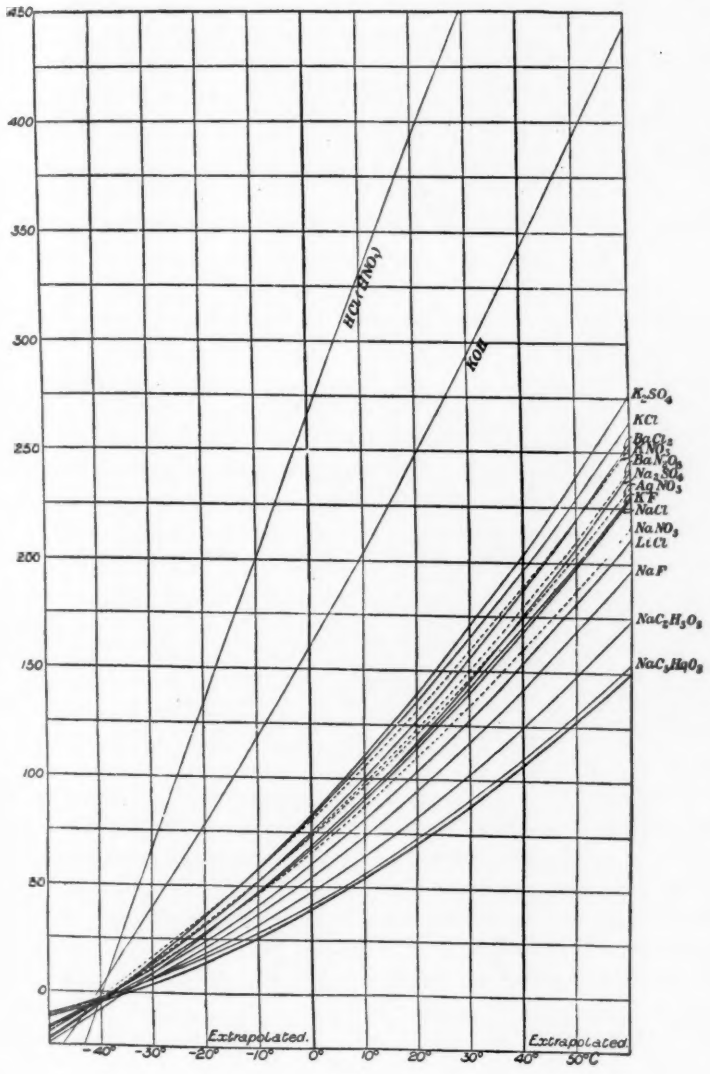
450
400
350
300
250
200
150
100
50
0
HCl (HNO3)
KOH
K2SO4
KCl
BaCl2
Ba(NO3)2
Ba2N2O5
Na2SO4
AgNO3
KF
NaCl
NaNO3
LiCl
NaF
NaC2H3O2
NaC3H5O3
Extrapolated.
Extrapolated.
-40°
-30°
-20°
-10°
0°
10°
20°
30°
40°
50°C

FIG. 19

die darin besteht, dass die gebundene Wassermenge von der Temperatur abhängt.

. . . "Ich halte die Hypothese, dass der Ionenwiderstand wesentlich durch die Menge mitgeführten Lösungsmittels bestimmt wird, jetzt schon für eine nicht zu bezweifelnde, und ich neige zu der Ansicht, dass die physikalische Chemie ernstlicher auf diese Vorstellung eingehen musste, als sie es bis jetzt tut."

Further relationships between the ionic conductances and the viscosity of the medium at different temperatures will be discussed in the next section.

The Size of Ions in Relation to the Physical Properties of Aqueous Solutions

In 1850 Sir George Stokes[107] considered the motion of a small sphere of radius, r, moving under a driving force, F, with a velocity, V, through a homogeneous viscous medium of viscosity, η, and deduced the following formula for its motion,

$$V = \frac{F}{6\pi\eta r} \tag{36}$$

This equation has received experimental confirmation in several cases, among which may be mentioned the experiments of H. S. Allen,[108] who has shown that the velocity of small bubbles of air rising through water or aniline agrees with that calculated by the above equation. Von Wogau[108a] has also recently applied the equation to the diffusion of metals in mercury.

Sutherland,[109] in 1902, attempted to apply Stokes's theory to the motion of the ions in solutions of electrolytes, under the assumption that they can be regarded as small spheres moving through a viscous medium, but abandoned the attempt because the theory required that the mobility of an ion should vary inversely with its radius, a condition which seemed to be contrary to the facts (the volume of the ion being assumed the same as that of the atom; see this review, page 415).

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[107] Stokes, Camb. Phil. Trans., 9, 58 (1850).

[108] Allen, Phil. Mag., [5], 50, 323 (1900).

[108a] R. 100; cf.. however, G. McP. Smith, Ann. Phys., 25, 252 (1908).

[109] Sutherland, Phil. Mag., [6], 3, 161 (1902).

This apparent discrepancy disappears (as we have seen, page 416) if the ion is surrounded by an atmosphere of the solvent, which moves with it through the solution. On this basis, therefore, the problem has recently been again attacked by W. R. Bousfield, who has considered the application of Stokes's theory to the motion of an ion, under the assumption that *the size of the ion is a function both of the temperature and of the concentration of the electrolyte.* The results of this consideration have recently appeared in two extensive papers [110, 111] by this author.[112]

It is by no means certain that it is justifiable to apply the Stokes's equation to the motion of an ion through a medium such as water, composed of particles whose dimensions are comparable with those of the ion itself. Nevertheless, Bousfield, starting with certain fundamental assumptions, has applied the Stokes equation to ionic mobilities, has developed numerous equations connecting the ionic volumes with various properties of the solution, and has found that the equations so derived are in agreement with the results of experiment. He reaches the conclusion that this agreement indicates the validity of his fundamental assumptions, the most important of which is the applicability of the Stokes equation. To the reviewer, however, it seems, as will be shown below, that these results tend, if anything, to disprove the assumption that the Stokes equation is applicable to ionic mobility. In the following treatment Bousfield's point of view and his results and conclusions are presented as completely as practicable within the limits of this review. In addition, the results and theories of other investigators of different phases of the subject are also presented, and the reviewer's interpretation is added in certain cases.

The Variation of the Size of Ions with the Temperature

If l_t and $l_{25°}$ represent the conductances of an ion (at infinite dilution) at $t°$ and 25°, respectively, it follows from Stokes's equation that

$$\frac{l_t}{l_{25°}} = \frac{r_{25°}\eta_{25°}}{r_t\eta_t} \quad \text{or} \quad \frac{r_t}{r_{25°}} = \frac{l_{25°}\eta_{25°}}{l_t\eta_t}. \tag{37}$$

[110] Bousfield, "Ionengrössen in Beziehung zur Leitfähigkeit von Electrolyten," Z. physik. Chem., **53**, 257–313 (1905); and

[111] Bousfield, "Ionic Size in Relation to the Physical Properties of Aqueous Solutions," Phil. Trans. [A], **206**, 101–59 (1906).

[112] See also papers by Carroll [Amer. Chem. J., **36**, 594 (1906)]; Pellat [Compt. rend., **144**, 902 (1907)]; and Carse and Laby [Proc. Camb. Phil. Soc., **14**, 1 (1907)].

If Stokes's theory is applicable to the motion of the ion, the right-hand member of the latter equation represents the radius of the hypothetical ionic sphere in terms of its radius at 25° taken as unity. This quantity will be called the "radion" (25°), following the nomenclature used by Bousfield. If the only effect of temperature upon the conductance of an ion is that due to the change in the viscosity of the medium, the product, $l_t\eta_t$, should be a constant for all temperatures. If we compute values of the quantity, $\frac{l_t\eta_t}{\eta_{25°}}$, for a series of temperatures, we shall obtain an idea of the magnitude of the factors, other than viscosity, which determine the mobility of an ion in aqueous solution. This quantity is obviously the conductance of the ion at $t°$ compared with that at 25° and corrected for the change in the viscosity of the medium (on the assumption of proportionality), thus eliminating that factor. In terms of Stokes's theory, this quantity is inversely proportional to the "radion," and will therefore serve as a measure of the change in radius undergone by the hypothetical ionic sphere with change in temperature (compared with its radius at 25° as unity).[118] The figures for the different ions will also serve as a basis for comparison of their volumes with one another according to this theory.

[118] That portion of Bousfield's first paper which dealt with this subject (R. 110, p. 274) was withdrawn by him in his second paper (R. 111, p. 105, note) for the reason that the data used by him were largely based on determinations of the conductivities of 0.001N solutions, and therefore included variations of the degree of ionization with the temperature. Moreover, they covered only a small temperature range (40°). Owing to the recent extensive investigations of A. A. Noyes and his co-workers [A. A. Noyes, "The Electrical Conductivity of Aqueous Solutions," Carnegie Inst. Pub. No. 63 (1907)], we are now, however, in possession of accurate data on the equivalent conductance at infinite dilution of a number of electrolytes at temperatures ranging from 0° to 306°. I have accordingly made use of these data in this section.

TABLE XV

VALUES OF $\frac{l_t \cdot \eta_t}{\eta_{25^\circ}}$, SHOWING THE DEVIATION FROM PROPORTIONALITY BETWEEN CONDUCTIVITY AND FLUIDITY

Ion.	0°.	18°.	25°.	50°.	75°.	100°.	128°.	156°.
K	80.8	76.4	74.8	71.0	68.0	65.8	63.6	62.2
Na	51.7	51.0	50.8	50.2	49.7	49.3	48.6	48.6
NH_4	81.5	77.0	75.4	71.5	68.4	66.2	63.8	62.6
Ag	64.8	63.4	62.8	61.3	60.4	59.8	58.7	58.3
½Ba	64.2	64.6	64.7	65.0	65.2	65.5	65.8	65.7
½Ca	61.0	61.3	61.4	61.7	61.8	62.0	61.9	62.2
⅓La	73.8	75.1	75.5	76.5	77.5	78.2	78.8	79.2
Cl	82.1	77.3	75.5	71.3	68.2	65.8	63.6	62.2
NO_3	80.8	73.0	70.8	64.4	60.1	56.9	53.7	51.7
Ac	40.7	41.0	41.0	41.2	41.2	41.3	41.2	41.3
½SO_4	80.6	80.0	79.7	79.3	78.5	78.2	77.5	77.4
½Ox	81.5	77.2	75.9	72.0	69.3	67.4	65.3	63.7
¼$Fe(CN)_6$	120.0	116.0	115.0	111.0	108.0	106.0	. .	. .
H	479.0	370.0	350.0	280.0	241.0	205.0	174.0	152.0
OH	209.0	202.0	192.0	175.0	157.0	140.0	126.0	115.0

Table XV contains the values[114] of this quantity for fifteen ions at eight different temperatures, ranging from 0° to 156°. For purposes of ready comparison, these data are plotted in Figure 20, temperatures being plotted as abscissæ and values of the quantity, $\frac{l_t \eta_t}{\eta_{25^\circ}}$, as ordinates.

In terms of Stokes's theory the curves shown in this figure would indicate that the ionic volumes of Na, Ag, and Ac (acetate) are nearly constant throughout this range of temperature; those of Ca and Ba decrease slowly, and that of La more rapidly with rising temperature; and those of the remaining ions, including H and OH (shown in the table, but not in the figure on account of the size of the scale), increase

[114] This table and the accompanying figure were prepared in this laboratory by Dr. J. Johnston and are included in a publication by A. A. Noyes and J. Johnston [Carnegie Inst. Pub. (1909)], which will appear shortly. I am indebted to Prof. A. A. Noyes for permission to use them in this review. In the preparation of this table the transference number for potassium chloride was taken as 0.50 at all temperatures above 50°. The values for the viscosity of water were interpolated, graphically, from the data of Thorpe and Rodgers and of de Haas (Landolt and Börnstein).

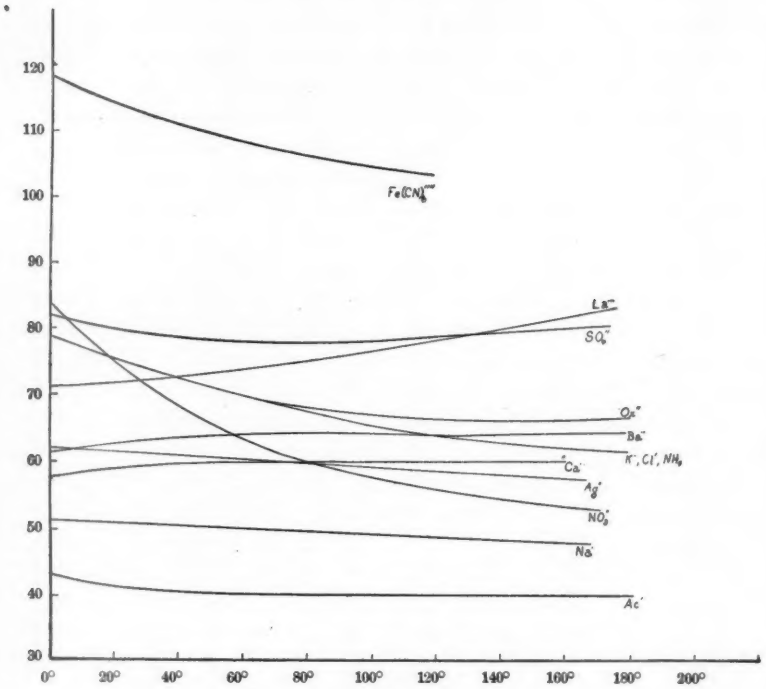

FIG. 20

with rising temperature. Bousfield seems inclined (R. 110, p. 277) to attribute these variations to corresponding changes in the degree of hydration. Such a conclusion requires that the degree of hydration of the majority of these ions increase, very rapidly in some instances, with rise in temperature, a conclusion which is at variance with most of the evidence regarding the sign of the heat of hydration.

The Variation of Ionic Size with Concentration. — According to Bousfield (R. 110, p. 273) the volume of an ion varies with the concentration of the electrolyte in a manner that may be expressed by the equation,

$$\frac{r_\infty}{r} = 1 + \varphi(h), \tag{38}$$

r_∞ and r being the radii of the hypothetical ionic spheres at infinite dilution and at the dilution h, respectively. $\varphi(h)$ denotes some function of the dilution h, the latter quantity being expressed as mols of water

per mol of solute. By combining this equation with Stokes's equation (36), it is shown to follow directly that the degree of ionization, γ (in solutions so dilute that the dielectric constant of the medium can be assumed to be the same as that of pure water), is expressed by the equation,

$$\gamma = \frac{\Lambda}{\Lambda_\infty} \cdot \frac{1}{F} \cdot \frac{1}{1 + f(h)}, \tag{39}$$

where F is the fluidity of the solution referred to that of water, at the same temperature, as unity.

The "true" value of γ, as given by this equation, cannot be calculated until the value of the unknown $f(h)$ is determined. To evaluate this function, the author assumes that the "true" value of γ is such that if it be substituted in the van't Hoff dilution law, *i. e.*,

$$\frac{\left(\frac{\gamma}{h}\right)^3}{\left(\frac{1-\gamma}{h}\right)^2} = K, \tag{40}$$

this law will hold exactly. Using Kohlrausch's values for the conductances of KCl solutions at 18°, the author combines equations (39) and (40) and evaluates $f(h)$ for this salt by a series of approximations, finally obtaining the result,

$$f(h) = 3.33h^{\frac{1}{2}}.$$

Values of γ for KCl solutions at 18°, calculated by the relation,

$$\gamma = \frac{\Lambda}{\Lambda_\infty} \cdot \frac{1}{F} \cdot \frac{1}{1 + 3.33h^{\frac{1}{2}}}, \tag{41}$$

are found by the author to satisfy the van't Hoff dilution law with a maximum error of 1 part in 2,000 up to a concentration of 0.2 molal. According to these results, equation (38) takes the form,

$$\frac{r_\infty}{r} = 1 + Bh^{\frac{1}{2}}, \tag{42}$$

where B is a constant characteristic of the ion in question. The author evaluates B for sodium, potassium, and chloride ions by means of a relation between this value and the transference number, which will be referred to later (page 434). With the equations so obtained, he computes a set of values showing the change of r^3 with the concentration. These values are given in Table XVI below, together with their sum

for each salt, this latter quantity being called the "ionic volume" of the salt in question and being denoted by the symbol I_v.

TABLE XVI

Salt.	P.	$r_K^3 \times 10^6$.	$r_{Cl}^3 \times 10^6$.	I_v.
KCl	0	3.692	3.569	7.261
	1	3.128	2.968	6.096
	3	2.627	2.448	5.075
	6	2.163	1.981	4.144
	Normal	2.029	1.852	3.881
NaCl	0	12.107	3.569	15.676
	1	10.848	2.876	13.724
	3	9.648	2.303	11.951
	Normal	8.578	1.852	10.430

It will be noticed that all of the foregoing deductions are based upon the two assumptions, (1) that the Stokes equation can be applied to the motion of the ion, and (2) that the van't Hoff dilution law is a true and accurate expression for the change of the ionization with the dilution; neither of which assumptions seems very plausible, although they have led the author to several very interesting empirical relationships, as we shall see in the following sections. A strong argument against the validity of these hypotheses is to be found in the results shown in the above table. On examining the values of r^3 for each ion, we notice at once that the volume of the ion, and therefore the size of the water atmosphere and consequently the degree of hydration in each case, increases rapidly with the dilution, as the Mass-Action Law requires that it should. But the Mass-Action Law also requires that the degree of hydration shall reach a constant value in dilute solution as soon as the activity (active-mass) of the water becomes constant. Now in a 1 per cent. solution of potassium chloride the activity of the water, as measured by its vapor pressure, has become practically constant, differing only about 0.4 per cent. from its value at infinite dilution. Consequently no great change in the degree of hydration can take place between this concentration and infinite dilution. The above table, however, shows a change of about *20 per cent.* in the volumes of the potassium and chloride ions over this range of concentration.

The Size of Ions in Relation to Density

Bousfield compares the "solution volume, V_s" (*i. e.*, the apparent molecular volume of the solute in solution calculated on the assumption that the volume of the water in the solution is the same as in the pure state), with the "ionic volume, I_v," on the assumption that (R. 111, p. 126) "the solution volume derived from density observations is a measure of the amount of contraction which takes place on solution, and therefore a measure of the amount of water entering into combination with the solute. The ionic volumes at different dilutions should be nearly proportional to the amounts of water in combination with the ions, if the volume of water is large compared with the volume of the ionic nucleus. Hence, if our theory is correct, we ought to find the solution volume approximately a linear function of the ionic volume of the pairs of ions in dilute solutions."

On comparison of these quantities for solutions of KCl and NaCl from 0 to 6 per cent. concentration, the relation between the two quantities is found to be a linear one. From this relation the author deduces a "rational-density formula," by means of which the density of a solution is expressed as a function of the quantity, I_v, the latter quantity being determined from conductivity measurements in the manner indicated. The densities of NaCl and KCl solutions calculated by this formula are shown to agree with the observed values within the experimental error (fifth decimal place) up to molal concentration.

The Size of Ions in Relation to Viscosity

We have already (this review, Sec. I, p. 408) discussed the viscosity of solutions in its relation to hydration from the standpoint of the law of mixtures. There remains only to mention briefly some of the theories and hypotheses which have been advanced with the idea of "explaining" the viscosity of solutions of electrolytes by variations in the size of the individual molecules of the components.

We have mentioned elsewhere the fact that the viscosities of the different ions exhibit the same anomaly as do their migration velocities. Euler[115] has, in fact, shown that the relation between the viscosity constant, k, of an ion and its equivalent conductance, l, can be expressed by the simple equation,

$$(k - 0.68)l = \text{const.} \qquad (43)$$

[115] Euler, Z. physik. Chem., **25**, 539 (1898).

The ions, NH_4, K, Rb, Cs, Tl, and NO_3, in aqueous solution tend to lessen the viscosity of the medium, so that solutions of many of their salts exhibit a lower viscosity than pure water. The electro-striction hypothesis, as proposed by Nernst and Drude [116] to explain this phenomenon of "negative viscosity," seems to be no longer sufficient to explain all the facts, since it has been shown by Wagner [117] and Mullenbein [118] that the same phenomenon occurs in non-conducting mixtures of organic liquids.

Most of the recent investigators [119] in this field have advanced some form of a hydrate hypothesis to explain the phenomenon, and such a hypothesis seems to accord well with the facts. This hypothesis is stated by Blanchard [120] as follows: "If now ions exist as hydrates, instead of simply as electrically charged atoms or radicals, they must be built up at the expense of the polymerized water molecules. Now it would seem highly probable that some of the hydrated ions, $M \cdot nH_2O$, might have a smaller mass, or, at least, a more symmetrical structure, than the $(H_2O)_x$ molecules of pure water. In such a case there might well be less friction to their motion than to that of the molecules of pure water. It is important to note that complexes between undissociated molecules of solute and molecules of solvent may be formed as well as the solvates of ions. With decreasing temperature the polymerization of water increases The formation, at least, of some of the possible polymers is attended by an expansion (which between 4° and 0° C. exceeds the normal contraction). Pressure thus will lessen the amount of polymerization and also lessen the viscosity, since polymerization obviously causes increased viscosity. At 32° C. the critical point is reached, where the polymerization of water is so slight that it is not decreased by pressure. The formation of solvates takes place to a lesser extent the higher the temperature. At higher temperatures there are also fewer molecules of polymerized water whose concentration will be diminished by the formation of hydrates. At 32° the effect of certain salts in lessening the viscosity, as well as that of pressure, becomes zero."

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[116] Nernst and Drude, Z. physik. Chem., **15**, 79 (1894).

[117] Wagner, Z. physik. Chem., **46**, 872 (1903).

[118] Mullenbein, Diss. Leipzig (1901).

[119] See, however, Jones, Carnegie Inst. Pub. No. **80**, 213 (1907); and Getman, J. Chim. Phys., **5**, 544 (1907); also Wagner (R. 117).

[120] Blanchard, "The Viscosity of Solutions in Relation to the Constitution of the Dissolved Substance," J. Amer. Chem. Soc., **26**, 1318 (1904).

Blanchard also adduces further evidence in support of this hypothesis. He finds (R. 120, p. 1330) that "addition of 2 and 4 mols, respectively, of ammonia to solutions of silver, copper, and zinc salts decreases very greatly the viscosity. Probably the degree of ionization of the metal-ammonia salts is slightly greater than that of the plain metal salts. This will, however, hardly account for the large decrease in viscosity, for Wagner [117] found, without taking ionization into account, that the viscosity of salts is, in general, very nearly equal to the sum of definite values assigned to each of the metallic and acidic atoms or radicals, respectively. . . . The only way, then, open to account for the decreased viscosity seems to be a decrease in size or an increase in symmetry of the salt molecules, or more especially of the positive ions of the salts (since ammonia is shown by migration experiments to form a part of that ion). If the positive ion consists solely of a metallic atom bearing an electric charge, combination with ammonia molecules cannot decrease its mass, and it is not easy to imagine that it can increase its symmetry. The only explanation, then, seems to be that metal ions in solution are hydrated; the hydrate-water is replaced by ammonia, which forms, with the ion, a more stable complex and one of less mass or greater symmetry, or both. It will be seen that this explanation of the lowering of viscosity of a metal salt solution by addition of ammonia is similar to the one offered earlier in this paper of negative viscosity."

Bousfield holds similar views. He remarks (R. 111, p. 129) "that it seems, *a priori*, probable that the *change of viscosity* caused by the introduction of foreign molecules into water would depend upon the number and size of the molecules so introduced. According to the theory postulated, an ion is a compound molecule, consisting of the ionic nucleus with its envelope of water molecules, as are also the un-ionized molecules of the solute. Hence, if the theory be true, we should expect to find a close relation between the viscosity of the solution and the number and size of these aggregates. The number of molecules depends upon the concentration, n, and the *size* upon the 'radions'; the product, $n(r_1 + r_2)$, should therefore be a measure of the joint effect of the introduced ions upon the viscosity in dilute solutions." In Table XVII are set out the concentrations and the observed and calculated viscosities for KCl and NaCl solutions. The "calculated" viscosities are computed from the formula,

$$\eta = a - bn(r_1 + r_2), \tag{44}$$

a and b being constants peculiar to the salt in question. The viscosity is thus seen to be a linear function of the quantity, $n(r_1 + r_2)$. The investigator also finds that a combination of the two viscosity equations for NaCl and KCl solutions yields an equation which expresses accurately the viscosity of various mixtures of these solutions. The author then proceeds to develop a general viscosity formula based upon his hypothesis. To follow this discussion further would lead too far from the subject of the present review, and the reader who is interested in further details should consult the original (R. III, pp. 134–142).

TABLE XVII

n.	η.	η.
	Observed.	Calculated.
0.0	0.010514	0.010514
0.1347	0.010504	0.010491
0.2712	0.010465	0.010470
0.4094	0.010445	0.010450
0.5493	0.010419	0.010430
0.8344	0.010393	0.010391
1.000	0.010374	0.010374

In speaking of the agreement between observed and calculated values in Table XVII, Bousfield remarks: "The agreement between observed and calculated values is sufficient to show that the *chief element* which determines the viscosity of the solutions is the product, $n(r_1 + r_2)$. . . . The results tend strongly to confirm the fundamental hypothesis as to the character of the magnitudes which we have called 'radions,' and which we derived from the conductivities by the application of the Stokes theorem and the van't Hoff law."

Is this conclusion justified? Bousfield's investigations have yielded some very valuable data on the viscosities and densities of aqueous salt solutions, and from his fundamental hypotheses he has derived formulæ for the density, the viscosity, and the conductivity of a salt solution and of a mixture of two salt solutions (R. III, p. 125). He has tested these formulæ by means of experimental data on KCl and NaCl solutions, and found that they express the facts accurately, in some cases (notably the density formulæ) even more accurately than any empirical formula previously proposed. Nevertheless, it is to be remembered that the funda-

mental hypotheses of this investigator — namely, the validity of Stokes's equation for ionic mobilities and the validity of the van't Hoff Dilution Law as applied by him — must be regarded as purely arbitrary hypotheses, of little *a priori* probability, and with the weight of evidence against them, as shown by some of the conclusions to which they have led the author (see pages 426, 428, and 434 of this review). What, then, is the explanation of the excellent agreement between the observed results and those calculated by the author's formulæ?

The reviewer is of the opinion that the probable explanation is that, although these formulæ are seemingly theoretical ones, they are, in reality, simply empirical expressions connecting the concentration and the property in question, the excellent agreement being produced by the number of arbitrary constants to be evaluated from experimental data. To illustrate, consider the viscosity formula, equation (44). This equation contains two constants (a and b) to be evaluated by experiment. If we substitute for r_1 and r_2 the expressions by which they are computed (R. 111, p. 125), we obtain

$$\eta = a - bn\left(\frac{1}{l_1(1 + B_1 h^{-\frac{3}{2}})} + \frac{1}{l_2(1 + B_2 h^{-\frac{3}{2}})}\right). \qquad (45)$$

This is an equation connecting, in a rather complicated manner, the viscosity, η, and the concentration, n, of a solution with the equivalent conductances of its ions, l_1 and l_2, and containing at least two constants to be determined by experiment. It is such an equation as would be obtained by combining two functions of the forms,

$$f(n, \eta) = 0 \text{ and } f(n, l) = 0, \qquad (46)$$

for each ion, and its agreement with the results of experiment is not, therefore, to be regarded as evidence either for or against the author's fundamental assumptions. Indeed the term, $Bh^{-\frac{3}{2}}$, in the above equation, which is the only portion of it which has any connection, even remotely, with Stokes's theorem and the van't Hoff dilution law as applied by the author, might be omitted entirely without seriously impairing the value of the equation as an accurate empirical relation.

Additional Relations

In addition to the relations which we have discussed, Bousfield finds, as one of the deductions from his hypotheses, that the Hittorf transfer-

ence number should be a linear function of the ratio of the radions. Using the ordinary values of transference numbers for KCl and NaCl, he finds that this conclusion agrees with the facts. This result is, however, if anything, an argument against his hypotheses, for, as we have seen (R. 120*a*), the Hittorf transference numbers which he used are not real transference numbers at all, since their calculation is based upon an erroneous assumption.

Neither, in the reviewer's opinion, can any importance be attached to the relation deduced by the author, that "the freezing-point depression is a linear function of the 'ionic volume,'" for further details of which reference must be had to the original (R. 111, p. 142).

The Determination of the Hydration of Ions by Transference Experiments

The description of this important method, together with the results obtained by it, has been given in a preceding communication,[120a] and will therefore not be discussed in this review.

SECTION III. MISCELLANEOUS METHODS

Hydration in Solution from the Standpoint of the Theories of the Constitution of Inorganic Compounds

A review of the subject of hydrates in solution which did not include a chapter dealing with the subject from the standpoint of the theory of Werner and that of Abegg and Bodländer would be incomplete. The subject of hydration in aqueous solution constitutes, however, only a small, if important, part of either of these theories, so that in the present review it will be necessary to assume, on the part of the reader, a familiarity with the general outlines of the two theories. The following presentation will, so far as practicable, be given in the author's own words.

The Theory of Werner.[121, 122, 123] — In 1893 Werner expressed the

[120a] This QUARTERLY, **21**, No. 3, 287 (1908).

[121] Werner, "Beitrag zur Konstitution anorganischer Verbindungen. 'V' Über den Zustand der Metallsalze in wässeriger Lösung," Z. anorg. Chem., **3**, 294 (1893).

[122] Werner, "Neuere Anschauungen auf dem Gebeit der anorganischen Chemie," Braunschweig (1905).

[123] Werner, "Zur Theorie der Basen," Ber. Chem. Ges., **40**, 4133 (1907).

opinion that combination with the solvent was a necessary precedent to electrolytic dissociation. This view seems to have been derived by this eminent investigator solely as a deduction from his general theory regarding the constitution of inorganic compounds, since at the time of its publication there was little evidence indicating that ions are hydrated, an ion being almost universally regarded simply as an atom or radical possessing an electric charge and maintaining an independent existence within the solution. Werner was therefore one of the first to suggest a hydrate theory of ionization.[124] His views are therefore particularly interesting at the present time.

According to Werner (R. 121, p. 294): "Wir haben, wie es schon früher formuliert wurde, die wasserhaltigen Salze nicht als MX + aq zu schreiben, sondern (Maq)X; also wasserhaltiges Chlorcalcium nicht $CaCl_2 + 6$ aq, sondern $Ca(H_2O)_6Cl_2$. Negative Radikale, welche sich in direkter Bindung mit dem Metallatom befinden, sind keine Jonen; damit ein negativer Rest als Jon wirken könne, ist als erste Bedingung die Bildung des Hydrates, also Bildung der Salze wasserhaltiger Metallradikale, erforderlich. . . .

"Nach der Anschauung, wie sie sich aus unseren Betrachtungen ergiebt, ist die Existenz von Hydraten in wässeriger Lösung nicht nur im Sinne der Hydrattheorie anzunehmen, sondern diese Hydrate bilden auch die erste unumgängliche Bedingung zur elektrolytischen Dissoziation. Wir haben in wässeriger Lösung als Jonen nicht Metallatome, sondern Metallatome umgeben mit sechs an sie geketteten Wassermolekülen, mit denen sie geradezu zusammengesetzte Radikale bilden. Damit wird nun auch klar, warum das elektrolytische Leitvermögen, die Dissoziation der Salze in so grosser Abhängigkeit steht vom Lösungsmittel. *Nur solche Lösungsmittel sind befähigt, elektrolytische Dissoziation zu bedingen, welche mit den Metallsalzen zu analogen Radikalen zusammentreten können,* so in beschränktem Masse Alkohole, wie aus der Existenz von Verbindungen wie $Ca(C_2H_5.OH)_6Cl_2$; $Ca(C_2H_5.OH)_6(NO_3)_2$ hervorgeht.

"Die nächste wichtige Frage, die sich aufwirft ist die nach der *Natur der Hydratbildung.* Dieselbe wird in präciser Form durch unsere Entwicklungen beantwortet. In jedem wasserfreien Salze haben wir direkte Bindung zwischen Metall und Säurerest anzunehmen. Das Wasser besitzt nun die Eigenschaft, je nach dem Metall mit grösserer oder geringerer Leichtigkeit sich zwischen Metallatom und Säurerest

[124] Cf. Ciamician, Z. physik. Chem., **6**, 405 (1890).

einzuschieben und so aus der direkten Bindung eine durch das Wassermolekül vermittelte indirekte Bindung zu schaffen.

"Die dadurch entstehenden Radikale, bestehend aus Metall und Wasser, können aber die verschiedensten Grade der Beständigkeit zeigen. Sie können in ihrer höchsten Form $M(H_2O)_6$ beständig sein, . . . , sie können aber auch, . . . in festem Zustande mit weniger Wasser auftreten. In wässeriger Lösung, wenigstens in verdünnter, werden sie wohl alle der Form $M(H_2O)_6$ entsprechen, und dies wird bedingt werden durch die Massenwirkung des Wassers.

"Diese Hydrate können aber auch in manchen Fällen nur in Gegenwart von viel Wasser als solche bestehen, was z. B. in den Kaliumsalzen der Fall zu sein scheint. Dieselben Krystallisieren meistens wasserfrei, leiten aber dennoch in wässeriger Lösung ausgezeichnet." . . .

"Zum Schlusse dieser Betrachtung wiederholen wir:

"*Die erste Bedingung zur elektrolytischen Dissoziation eines Salzes ist die Fähigkeit seines Metallatoms, sich mit einer bestimmten Anzahl von Wassermolekülen zu einem Radikal zu verbinden, in dem wir uns die Wassermoleküle so angeordnet zu denken haben, dass eine direkte Bindung zwischen dem Metallatom und dem Säurerest nicht mehr eintreten kann.*"

Werner's views regarding the mechanism of the process of ionization as a phenomenon of hydration are expressed as follows (R. 121, p. 323): "Denken wir uns das Metallatom als Kugel, die sechs mit demselben direkt verbundenen Komplexe in einer ersten um dasselbe beschriebenen Sphäre sich befindend, und die anderen ausserhalb dieser ersten Sphäre sich befindenden Reste als in einer zweiten Sphäre liegend, so können wir für sämtliche betrachtete Verbindungen den allgemeinen Satz aufstellen: Die Valenz des durch das Metallatom und die sechs mit ihm verbundenen Komplexe der ersten Sphäre gebildeten Radikals (MA_6) ist gleich der Differenz der Valenz des Metallatoms und der Valenz der einwertigen Gruppen der ersten Sphäre, ganz unabhängig von der in der ersten Sphäre vorhandenen Moleküle wie H_2O, NH_3 u. s. w.

"Dies wird sofort an folgenden Beispielen klar werden:

$$(Co(NH_3)_6)\ 3 - 0 = 3 :\ (Co(NH_3)_6)X_3$$

$$\left(Co\begin{matrix}(NH_3)_3\\(NO_2)_3\end{matrix}\right)\ 3 - 3 = 0 :\ \left(Co\begin{matrix}(NH_3)_3\\(NO_2)_3\end{matrix}\right)$$

$$\left(Co\begin{matrix}(NH_3)_2\\(NO_2)_4\end{matrix}\right)\ 4 - 3 = 1 :\ \left(Co\begin{matrix}(NH_3)_2\\(NO_2)_4\end{matrix}\right)K$$

u. s. w.; dieser Satz besitzt allgemeine Gültigkeit.

"Es besteht also ein charakteristischer Unterschied in der Wirkungsweise von Wasser- und Ammoniakmolekülen und derjenigen einwertiger Radikale. . . .

"Die Wirkungsweise der Moleküle wie NH_3, H_2O u. s. w. ist eine spezifisch ganz eigenartige; sie kann etwa folgendermassen definiert werden: Diesen Molekülen kommt die Eigenschaft zu, die Wirkungstellen der Affinitätskraft des Metallatoms aus der ersten Sphäre, in der sie im allgemeinen zur Thätigkeit gelangt, in eine vom Metallatom weiter entfernte Sphäre zu verlegen.

"Um dies durch eine Vorstellung, welche aber keine Beziehung zwischen den beiden Phänomenen andeuten soll, zu versinnlichen, sei diese Wirkungsweise folgendermassen mit einem elektrischen Phänomen verglichen. Denken wir uns das Metallatom als Kugel, geladen mit positiver Elektrizität, und die Wassermoleküle als neutraler Mantel um dieselbe gehüllt, so wird sich in diesem neutralen Mantel negative Elektrizität auf der inneren Mantelfläche ansammeln, wahrend auf der äusseren sich positive ansammeln wird. Die äussere Mantelfläche wird also nach dem ausserhalb gelegenen Raume nämliche Mengen positiver Elektrizität zur Wirkung bringen können, wie vorher das Metallatom. War der Mantel nicht vollständig neutral, sondern z. B schwach positiv, so wird dadurch die nach der zweiten Sphäre hin zur Wirkung kommende positive Elektrizitätsmenge um den gleichen Betrag verstärkt erscheinen.

"Ganz in derselben Weise erscheint nun die Wirkungsweise der Wasser-und Ammoniakmoleküle. Sie übertragen die Affinität nach einer weiter ab vom Metallatom liegenden Sphäre, und das Ammoniak, welches anscheinend einen etwas positiven Komplex darstellt, besitzt die Eigenschaft, gleichzeitig mit dieser Übertragung den positiven Charakter der Affinitätswirkung zu verschärfen. Wir haben früher aus der Betrachtung der Metallsalze in Lösung den Schluss gezogen, die erste Bedingung zur elektrolytischen dissoziation eines Salzes sei die Fähigkeit seines Metallatoms sich mit einer bestimmten Anzahl von Wassermolekülen zu einem Radikal zu verbinden. Wir haben uns nun eine Vorstellung gebildet über die Rolle dieser Wassermoleküle. Denken wir uns nun das Salz eines solchen Hydrats $M(H_2O)_6$, z. B. $M(H_2O)_6X_3$ in Wasser gelöst. Da dem Wasser schon die Fähigkeit zukam, die Wirkung der Affinitätskraft aus der ersten Sphäre in eine zweite zu verlegen, so ist nichts natürlicher als anzunehmen, dass die Wassermoleküle, von denen das Hydratsalz $M(H_2O)_6X_3$ in seiner Lösung in

Wasser umgeben ist, auch wieder die Eigenschaft besitzen werden, die Wirkung der Affinitätskraft, welche im Hydrat zunächst in einer zweiten Sphäre zur Thätigkeit gelangt, auch noch auf eine weitere Entfernung zu übertragen, indem sie um den ersten neutralen Mantel einen, allerdings nur in Gegenwart von überschüssigem Wasser beständigen zweiten neutralen Mantel bilden werden, um diesen zweiten einen dritten u. s. w. Die Folge davon wird eine vollständige Trennung des positiven und negativen Komplexes des Salzes sein, wir gelangen auf diesem Wege zur elektrolytischen Dissoziation der Salze in wässeriger Lösung und gleichzeitig zur Vorstellung, dass diese Dissoziation durch die Eigenschaft des Wassers, als Kraftüberträger zu wirken, bedingt wird." See also a more recent paper (R. 123, p. 4133).

An interesting application of Werner's theory is the explanation of the peculiar behavior, in solution, of the green and violet hydrates of chromium chloride. These unique compounds seem to belong to a class of hydrates of which few examples are known. The grayish blue hydrate, $CrCl_3 \cdot 6H_2O$, gives a violet solution in water. All three chlorine atoms are ionized in this solution, as shown by conductivity and cryoscopic measurements and by the fact that the chlorine is completely precipitated by silver nitrate. This hydrate corresponds to the hexammonia complex, $[Cr(NH_3)_6]Cl_3$, and its formula should therefore be written, $[Cr(H_2O)_6]Cl_3$, according to Werner's theory. The green hexahydrate gives a green aqueous solution, in which only one of the chlorine atoms is ionized, and consequently only part of the chlorine is precipitated in the cold by silver nitrate. In terms of Werner's theory, these relations are expressed by the formula,

$$[Cr^{Cl_3}_{(OH_2)_4} + 2H_2O]Cl.$$

On standing, the green solution changes slowly into the violet one, the reaction being

$$[Cr^{Cl_3}_{(OH_2)_4}]^{+} + 2H_2O = [Cr(H_2O)_6]^{+++} + 2Cl^{-}.$$

This reaction seems to resemble that of the hydration of milk sugar in that it is a slow hydration in solution accompanied by an intramolecular rearrangement (cf. this review, Sec. I, p. 394). In addition to these two forms the theory provides for the existence of the forms,

$$[Cr^{Cl_3}_{(OH_2)_3} + 3H_2O] \quad \text{and} \quad [Cr^{Cl}_{(OH_2)_5} + H_2O]Cl_2,$$

the latter having two ionizable chlorine atoms and the former none.

The corresponding compounds in the case of the sulphate have been prepared and studied recently by Colson,[125] the results being in full accord with the theory of Werner.

The Theory of Abegg and Bodländer.[126, 127, 128] — (R. 128, p. 1.) "Man muss . . . bei anorganischen Verbindungen ausser von einer Affinität zwischen Atom und Atom noch von einer solchen zwischen Atom und elektrischer Ionenladung sprechen, welch letztere als *Elektroaffinität* bezeichnet werden möge.

"Die *Zersetzungsspannung* eines Ions, welche die elektromotorische Kraft angiebt, die zur Trennung der Ladung vom Ion aufgewendet werden muss, ist zwar kein genaues Maass für die *Elektroaffinität* des Ions, da sich keine isolierten Atome, sondern Molekeln abscheiden; sie giebt aber im Verein mit Betrachtungen über Löslichkeit und Dissociationszustand von Elektrolyten, sowie die Fähigkeit zur Komplexbildung ein annäherndes Maass für die Reihenfolge der Ionen nach ihrer Elektroaffinität. . . .

"Ich möchte nun ausführen, dass die *Komplexsalzbildung* mit der Elektroaffinität in nächstem Zusammenhange steht, und schicke dazu folgende Definition voraus:

"*Eine komplexe Verbindung ist eine solche, deren eines Ion aus einer Molekularverbindung zwischen einem einzeln existenzfähigen Ion ('Einzelion') und einer elektrisch neutralen Molekel ('Neutralteil') besteht.* . . .

"Besonders als Neutralteil geeignet ist das Wasser, und in der That spricht vieles dafür, dass die Ionen namentlich von geringer Elektroaffinität, und zwar sowohl Anionen als Kationen, hydratisiert sind. . . .

"Die Thatsache, dass die komplexen Ionen stärker als die Einzelionen sind, lässt folgende physikalische Erklärung zu:

"Durch die Neutralteiladdition wird das Volum und damit die Oberfläche des Ions vergrössert, so dass die pro Valenz stets gleiche Ionenladung auf dem Komplex ein geringeres elektrisches Potential erhält als auf dem Einzelion; das höhere Potential bedingt aber eine grössere Tendenz des Ions, sich zu entladen, die also durch Komplex-

[125] Colson, Ann. chim. phys., **12**, 433 (1908).

[126] Abegg and Bodländer, "Die Elektroaffinität, ein neues Prinzip der chemischen Systematik," Z. anorg. Chem., **20**, 453 (1899).

[127] Abegg, "Die Valenz und das Periodische System. Versuch einer Theorie der Molekularverbindungen," *ibid.*, **39**, 330 (1904).

[128] Abegg, "Über Komplex Salze," Z. Electrochem., **6**, 92 (1899).

bildung verringert wird, was mit der grösseren Elektroaffinität gleichbedeutend ist."

An example of this occurs in the case of the alkali-ions, where, as we have seen (this review, Sec. II, p. 416), the degree of hydration increases in the series, K, Na, Li. According to Abegg and Bodländer (R. 126, p. 491), "Eine solche Verschiedenheit des Hydratationsgrades müsste ihrerseits nach den obigen Entwickelungen mit der verschiedenen Stärke der Ionen in Zusammenhang stehen, indem das schwächste Ion das grösste Additionsvermögen (= Bestreben, sich zu verstärken) besitzen wird. In der That ist das Lithium ein schwächeres Ion als Natrium, und das Kalium stärker als beide, was sich ohne Belege im einzelnen schon aus ihrem gesamten chemischen Verhalten bestätigt."

Abegg's views concerning the nature of the equilibria in a solution of an electrolyte are expressed as follows (R. 127, p. 359): "Ganz allgemein stellt eine Elektrolyt-Lösung nach unseren Anschauungen, . . . einen Gleichgewichtszustand zwischen folgenden Affinitäten dar:

"1. Ionen + Ionen $\rightleftarrows$ (undissoziierte Molekeln).

"2. Ionen + Lösungsmittel $\rightleftarrows$ (Ionen-Lösungsmittelverbindung).

"3. Undissoziierte Molekeln + Lösungsmittel $\rightleftarrows$ (deren Verbindung).

"Offenbar sind schlechtdissoziierende Lösungsmittel solche, die eine geringe Affinität (2) zu Ionen haben; und vice versa. Ist nun die Ionenbildungstendenz (1) eines Salzes stark, so muss die Affinität (3) seines undissoziierten Teils zum Lösungsmittels ohne wesentlichen Einfluss bleiben, da er im Verhältnis zu seinen Ionen keine hohen Konzentrationen erreichen kann. Diesen Fall repräsentieren die Lösungen aller starken Elektrolyte. Ihre Löslichkeit wird also wesentlich bestimmt durch die Affinitat ihrer Ionen zum Lösungsmittel, ist demgemäss gross in Wasser, gering in schwachdissoziierenden Medien."

Mention should also be made of certain other theories which involve hydration in solution as one of their deductions. Thus Euler[129] regards ammonium hydroxide as an amphotoric electrolyte and writes its formula, $H_3N \begin{matrix} \nearrow H^+ \\ \searrow OH^- \end{matrix}$; and from analogy thereto the formula for water is written, $H_2O \begin{matrix} \nearrow H^+ \\ \searrow OH^- \end{matrix}$, with one tetravalent oxygen atom. Carrying

[129] Euler, Arkiv. Kemi-Min. K. Svenska Veten.-Akad., Stockholm, 1, 203 (1904).

the analogy still further, he assigns to the silver-ammonia-ion and the silver-ion in aqueous solution the formulæ,

$$[Ag(NH_3)_2]^+ \quad \text{and} \quad [Ag(H_2O)_2]^+.$$

Similarly the nickelous, cupric, and cobaltic ions in aqueous solution are assigned the formulæ,

$$[Ni(H_2O)_4]^{++}, \quad [Cu(H_2O)_4]^{++}, \quad \text{and} \quad [Co(H_2O)_6]^{+++}.$$

In support of the formula assigned to the silver-ion the author adduces the following evidence. If the formula assigned to the silver-ion is correct, the addition of ammonia to a solution of silver nitrate simply results in the replacement of two water molecules by two ammonia molecules. The masses of the two ions are almost the same (143 and 141), and from the similarity in the structure of water and ammonia it is not unreasonable to suppose that the volumes are also nearly the same. The new ion ought, therefore, on this view, to have nearly the same equivalent conductance as the original silver-ion. The conductances are, according to Euler,

Silver-ion 51.8,

$[Ag(NH_3)_2]^+$ 52.0.

Similarly the viscosity coefficients of the two solutions should be nearly the same. They are given by Euler[130] as

¼ N. silver nitrate 1.018,

¼ N. $Ag(NH_3)_2NO_3$ 1.020.

Somewhat similar are the interesting views of Hantzsch[131] regarding the nature of ionization in solution. He regards an acid in solution as a "hydronium" salt, thus,

$$HCl + H_2O = [H_2O.H]Cl = (H_3O)^+ + Cl^-;$$

from analogy to the corresponding reaction by which an ammonium salt is formed from an acid and ammonia,

$$HCl + NH_3 = NH_3.HCl = (NH_4)^+ + Cl^-.$$

This last reaction corresponds to the process of ionization of an ammo-

[130] Compare, however, Blanchard's results (R. 120, p. 1330), which fail to confirm Euler's formulæ for the other ions when the same mode of reasoning is followed.

[131] Hantzsch, Z. physik. Chem., 61, 307 (1907).

nium salt in liquid ammonia, in which solvent the behavior of ammonium salts resembles the behavior of acids in aqueous solution, as shown by Franklin and Kraus.[132]

Mention may also be made of a recent paper by Lowry,[133] where the subject of electrolytic dissociation in general is discussed from the standpoint of a "solvate" theory.

The question of hydrated ions in its relation to the electron theory is considered briefly by Fournier-D'Albe.[134] According to the views of this author, when ionization takes place the two atoms separate, the negative atom or group taking one of the electrons from the positive atom or group. "The two ions so produced act as condensation nuclei, and each attracts molecules of the solvent about itself and becomes hydrated," the action resembling that which takes place in an ionized gas.

Hydration and Color Changes in Solution

Owing to the recent appearance of an excellent and exhaustive review of the subject of light absorption in solutions of electrolytes, under the authorship of G. Rudorf,[135] any attempt at an extended treatment of this phenomenon and of its relation to hydration in the present discussion would be superfluous. The reader who is interested in this phase of the subject should therefore refer to Rudorf's treatment, especially to pages 473–482 of Part I and to pages 390–411 of Part II. Since, however, this method has yielded one of the most satisfactory and conclusive *proofs* of the existence of hydrates in aqueous solution in certain instances, it seems desirable to include here a description of the experimental evidence and the theoretical interpretation which has led to this conclusion. This evidence is furnished by the experiments of Vaillant[136] and by those of Lewis[137, 138] on the color

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[132] Franklin and Kraus, Amer. Chem. J., **23**, 305 (1900).

[133] Lowry, "An Application to Electrolytes of the Hydrate Theory of Solutions," Trans. Farad. Soc., **2**, 197 (1905).

[134] Fournier-D'Albe, "The Application of the Electron Theory to Electrolysis," Chem. News, **95**, 28 (1907); Engineering, **83**, 87 (1907).

[135] G. Rudorf, Jahb. Rad. u. Elec., **3**, 422 (1907), and **4**, 380 (1908).

[136] Vaillant, Ann. chim. phys. [7], **28**, 257 (1903).

[137] Lewis, Z. physik. Chem., **52**, 224 (1905); also

[138] Bureau of Gov. Lab's P. I. Pub. No. **30**, 21 (1905).

changes produced in solutions of cobalt and copper salts by the addition of a second solute to the solution. The experiments of Vaillant, while no less conclusive, do not furnish so direct and simple a demonstration of the point in question as do those of Lewis, which we shall therefore consider here.

The changes in color undergone by solutions of cobalt and of copper salts when they are diluted were attributed by Wiedemann [139] to the gradual hydration of the salts. This explanation was later succeeded by that of Ostwald, according to which the color changes were attributed to ionization, the ions and undissociated molecules being supposed to have different colors. More recently Donnan and Basset [140] and Kohlschütter [141] have shown the presence of colored complex ions (such as $CoCl_4^{--}$, for example) in these solutions, and the color changes taking place on dilution were attributed by Donnan to the formation and dissociation of these complex ions. Lewis has shown that neither of these last two theories is alone sufficient to explain the facts, but that water enters into the reaction which produces the color change.

According to the three different explanations we should have,[142] respectively, equilibria of the following three types existing in the solution:

$$CuBr_2 \text{ (brown)} \rightleftharpoons Cu^{++} \text{ (blue)} + 2Br^{-}. \qquad (a)$$

$$CuBr_4^{--} \text{ (brown)} \rightleftharpoons CuBr_2 \text{ (blue)} + 2Br^{-}. \qquad (b)$$

$$CuBr_2 \text{ (brown)} + nH_2O \rightleftharpoons Cu(H_2O)_n^{++} \text{ (blue)} + 2Br^{-}. \qquad (c)$$

The color change in the last case may of course be due chiefly, not to a change from the anhydrous undissociated salt to the hydrated ion, but to a change from a hydrate with less water to one with more; but in any case the argument would be the same, so we may assume the above reaction for the sake of simplicity.

According to equations (*a*) and (*b*), the Mass-Action Law requires that the equilibrium between the brown and the blue constituents shall, at constant temperature, depend only upon the concentration of the bromide-ion. According to the equation (*c*), however, the equilibrium depends not only upon this factor but also upon the active mass of

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[139] Wiedemann, Report Brit. Assoc., p. 346 (1887).

[140] Donnan and Basset, Trans. Chem. Soc., **81**, 939 (1902).

[141] Kohlschütter, Ber. Chem. Ges., **37**, 1168 (1904).

[142] See Lewis, Z. physik. Chem., **56**, 223 (1906).

the water. In order to decide between these two hypotheses, Lewis (R. 138, p. 25) made the following series of experiments: "The same quantity of cupric bromide was added to 10 c.c. of a thrice-normal solution of each of the following bromides, KBr, NH_4Br, NaBr, LiBr. In these solutions the concentrations of bromide-ion are nearly alike, being somewhat greater in the case of KBr, somewhat less in the case of LiBr. If this were the only factor determining the color, we should expect the solution in KBr to be the most brown, that in LiBr the least.

"The facts are just the opposite. The NH_4Br and NaBr solutions have nearly the same color, that of KBr is less brown, while the LiBr solution is very much browner. In all these solutions the blue is so faint, as compared with the brown, that the relative brownness of the solutions can be found by means of a colorimeter. Columns of LiBr, NaBr, and KBr solutions, respectively 14, 18.5, and 20 mm. thick, appeared equally brown.

"These experiments were repeated several times, a different quantity of cupric bromide being used in each instance. The results were the same. A small change in the concentration of cupric bromide in any solution changes only the density of the color, but not its character. It is obvious that something influences the color besides the concentration of the bromide-ion. . . .

"Similar experiments were made with cupric chloride and solutions of the five chlorides, KCl, NH_4Cl, NaCl, LiCl, and HCl. Here the colors are not so pronounced as in the previous case. All the solutions are green. No difference could be detected in the first three, but the LiCl solution was decidedly greener and the HCl solution still more so." When the chlorides of the alkaline earth metals were used, the influence upon the color was found to be much greater, the order being $SrCl_2$, $CaCl_2$, $MgCl_2$, $BeCl_2$.

"All these experiments were repeated, using cobaltous chloride in place of cupric. The color differences here are less marked. The solutions of the chlorides of the first group all had practically the same red color with a tinge of blue. But in the second group the solutions were a more decided purple and arranged themselves in the same order as before, that is, $BeCl_2$ gave the solution with most blue in it."

As regards their relative effects upon the color changes, therefore, these various salts arrange themselves in the same order as is exhibited by their effects upon the activity (active-mass) of the water, as we have seen in Section I, page 364. Since, therefore, changes in color are

produced when the activity of the water alone is changed, we must conclude that water enters into the reaction which causes the color change. This result, taken in conjunction with the experiments of Donnan and Basset, referred to above, renders it probable that equilibria of the following type exist in solutions of cobalt and copper salts.

$$\underset{red}{CoCl_2(H_2O)_n} + mCl^- \rightleftharpoons [\underset{blue}{CoCl_2(Cl)_m(H_2O)_p}]^{(m)-} + (n-p)H_2O.$$

Kohlschütter (R. 141, p. 1168), in conformity with Werner's theory, expresses the reaction producing the color change in copper chloride solutions as follows:

$$[Cu^{Cl}_{(H_2O)_3}]^+ + H_2O \rightleftharpoons [Cu(H_2O)_4]^{++} + Cl^-.$$

These formulæ are based upon the analogy with the corresponding ammonia complexes, whose existence has been demonstrated, copper being assigned the coördination number, 4.

The Effect of Salts upon Reaction Velocities in Aqueous Solution

In a recent investigation R. J. Caldwell[143] has shown that the velocity of the inversion of cane sugar by acids in aqueous solution is, for a given strength of acid, much more nearly proportional to the concentration of the sugar if the concentration is expressed as mols per 1,000 grams of water instead of as mols per liter of solution. Employing, therefore, the weight-normal method of expressing concentration, he studied the effect of various chlorides upon the velocity of inversion of cane sugar by hydrochloric acid, and found in each case a marked acceleration in the rate of the inversion. To explain this phenomenon the author assumes that the salt is hydrated in solution, and thus by the removal of a portion of the water from its rôle as solvent exerts a "concentrating effect" upon the sugar; hence the acceleration in the rate of inversion. To determine the "average hydration" for the salt in question, it is only necessary, according to the author, to find by experiment how much water must be added to the solution containing the salt in order to restore the velocity constant to its original value. The author does this for a number of chlorides and obtains the results shown in Column II of Table XVIII.

[143] Caldwell, Proc. Roy. Soc., London, **78**, 290 (1906).

TABLE XVIII

"AVERAGE HYDRATION" OF SALT

Salt added.	I. Me. Ac.	II. Sugar.
KCl	8 H_2O	10 H_2O
NH_4Cl	5 H_2O	10 H_2O
NaCl	10 H_2O	13 H_2O
$BaCl_2$	18 H_2O	19 H_2O
$CaCl_2$	20 H_2O	22 H_2O
CH_3COOH	. .	1 H_2O
$AgNO_3$	. .	5 H_2O
NH_4NO_3	−2 H_2O	7 H_2O
KNO_3	1 H_2O	8 H_2O
$NaNO_3$	3 H_2O	11 H_2O
$LiNO_3$	. .	13 H_2O
$SrNO_3$	5 H_2O	18 H_2O
$CaNO_3$	7 H_2O	. .

R. Wymper [144] has recently made a similar investigation of the effect of nitrates upon the rate of inversion of cane sugar solutions by nitric acid. His results also appear in Table XVIII, Column II. In both of these investigations the concentration of the salt was about 1 mol per 1,000 grams of water. The effects of certain nonelectrolytes were also studied by these investigators. Glycerol and, to a greater degree, ethyl alcohol were found to exert a marked retardation upon the rate of inversion, while milk sugar was found to be practically without effect.

This work was still further extended by H. E. Armstrong and J. A. Watson,[145] who studied in a similar manner the effects of salts upon the rate of the hydrolysis of methyl acetate by hydrochloric and nitric acids. They found an acceleration in most cases in the presence of the salt and attributed it to the hydration of the salt. Their values for the "average hydration" of the various salts investigated are shown in Column I of Table XVII. The effects of the initial presence of the products of the hydrolysis — methyl alcohol and acetic acid — were also tried, and the former found to be practically without effect, while the latter had a distinctly accelerating action.

[144] Wymper, Proc. Roy. Soc., London, **79**, 576 (1907).

[145] Armstrong and Watson, Proc. Roy. Soc., London, **79**, 586 (1907).

To this same class belongs the recent investigation of E. H. Rennie, A. J. Higgin, and W. T. Cooke,[146] who studied the effect of the presence of various nitrates upon rate of solution of copper in nitric acid. Of the nitrates studied, that of sodium, and to a greater degree that of lithium, was found to exert a marked accelerating effect upon the rate of solution. Potassium nitrate was without effect, while cæsium and rubidium nitrates retarded the rate of solution. Beginning, therefore, with the nitrate producing the greatest acceleration, these salts arrange themselves in the following order: Li, Na, K, Rb, Cs. The order is here the same as found by Wymper for the effects of these salts upon the rate of inversion of cane sugar, and is attributed by the authors to the same cause, namely, the "concentrating effect" exerted by the salts in virtue of their hydration. The authors conclude that "these results afford additional evidence that the process of solution is accompanied by the combination of the solute with the solvent."

Without in any way questioning the importance of the investigations just described or of the value of the data obtained,[147] it is scarcely possible to agree with the interpretation placed by the investigators upon their results. Although several theories have been advanced to explain the neutral-salt-action, the question is still very much an open one, and the accumulation of further accurate data in this field is very desirable; but it is scarcely probable that it will ever yield *reliable* evidence concerning the complexity, or even the existence, of hydrates in aqueous solution. We have already noted and discussed (see Section I) the difficulties in the way of using an *equilibrium* (even in a *homogeneous binary* system) for the purpose of studying hydration in solution. In the method just considered the authors propose, however, to use the *rate* of a reaction and that in a *three-component* (and in the last instance even a *heterogeneous*) system as a basis not only for studying relative hydrations in solution, but even for calculating the complexity of such hydrates.

Conclusion

In concluding this review it seems desirable to emphasize again certain of the more important features. When we examine the various

[146] Rennie, Higgin, and Cooke, J. Chem. Soc., 93, 1162 (1908).

[147] Compare, however, Senter [Trans. Farad. Soc., 3, 163 (1907)], who, from his own experiments and from those of Arrhenius, Spohr, Kay, and others, finds that "the accelerating effect of neutral salts is practically independent of the nature of the salt."

methods which have been applied to the solution of this question, we find three methods which are distinguished from the rest by their freedom from arbitrary assumptions, and whose results are therefore to be regarded as constituting definite proof of the existence of hydrates in aqueous solutions.

(1) One of these is the solubility method. The existence of a solid hydrate in equilibrium with its solution is conclusive proof that the same compound is present in the solution. We have seen, moreover, that the shape of the solubility or melting-point curve is a fair indication of the stability of the compound in the liquid phase. This method is restricted to a definite hydrate in each instance, and so far as any quantitative conclusions are concerned it is necessarily confined to saturated and very concentrated solutions. At present it does not appear to be capable of further development on the quantitative side, except possibly in certain instances where the solute is found to exhibit a "maximum rate of solution."

(2) Certain copper and cobalt salts in aqueous solution undergo color changes when the solution is diluted. We have seen that the water enters into the reactions which produce these color changes. The solute is consequently hydrated in solution. This method is necessarily restricted to a few cases, and has not yielded any results of a quantitative nature.

(3) The third method deals with the hydration of ions in aqueous solution and is based upon transference measurements. This method is superior to either of the others, because it can be applied to a large number of solutions at different concentrations and temperatures, and because it yields quantitative results on the relative degrees of hydration of the ions. When carried out in the manner indicated (*i.e.*, by combining Hittorf transference numbers with those obtained by the method of moving boundaries) it offers a most promising field for future research (R. 120*a*).

In addition to these three methods, there exists, as we have seen, a large number of methods, the results of which, taken individually, cannot be regarded as conclusive, owing to certain assumptions which they involve. Taken together, however, and in conjunction with the three methods above mentioned, they constitute a strong body of evidence concerning the existence and nature of complexes between solute and solvent in solution. Of these methods the one which promises the most for future investigation is the method depending upon the lower-

ing of the vapor pressure. The evidence thus far available indicates that the vapor-pressure law, $\Delta p = p_o N'$, is applicable to aqueous solutions of "normal" solutes up to comparatively high concentrations. If this conclusion is confirmed by future research, we may hope to obtain fairly reliable quantitative data on the total hydration of non-electrolytes (and possibly of electrolytes) in solution. The method is sufficiently promising to make the accumulation of accurate vapor-pressure data for moderately concentrated solutions highly desirable.

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A SYSTEM OF QUALITATIVE ANALYSIS FOR THE COMMON ELEMENTS[1]

PART IV. ANALYSIS OF THE ALKALINE-EARTH AND ALKALI GROUPS

BY WILLIAM C. BRAY

INTRODUCTION

THE earlier parts of this system of analysis have dealt with the "Preparation of the Solution,"[2] the "Analysis of the Silver, Copper, and Tin Groups,"[2] and the "Analysis of the Aluminum and Iron Groups."[3] The present part treats of the analysis of the two remaining groups of metallic elements, which include barium, strontium, calcium, magnesium, sodium, potassium, and the rarer element, lithium. The general purposes of the investigation, the method of presentation, and the meaning of the abbreviations used have been described in the Introduction to the first paper.[2]

GENERAL DISCUSSION

In the method of analysis here presented magnesium is precipitated by ammonium carbonate, together with the other alkaline-earth elements (barium, strontium, and calcium), instead of being separated from them by this reagent. This somewhat radical modification of the usual process was made possible by the knowledge that magnesium separates out completely as a double ammonium magnesium carbonate when the solution is cold, and is concentrated with respect

[1] Copyright, 1909, by ARTHUR A. NOYES.

[2] A. A. Noyes and W. C. Bray, this QUARTERLY, **19**, 191 (1906).

[3] A. A. Noyes, W. C. Bray, and E. B. Spear, this QUARTERLY, **21**, 14 (1908).

to both ammonium carbonate and ammonium hydroxide (the effect of the latter substance being to drive back the hydrolysis of the ammonium carbonate). Some time is, to be sure, required for complete precipitation, but this may be reduced from several hours to less than half an hour by the addition of alcohol. This method was developed in connection with experiments that were made to determine the proper conditions for precipitating calcium, strontium, and barium completely, in the course of which it was found not possible to attain this result by increasing the concentration of the ammonium carbonate without at the same time causing the precipitation of magnesium when much was present. It was, however, afterwards found that Schaffgotsch,[1] as early as 1858, had recommended this method of separating magnesium quantitatively from the alkali elements, and an improved process has been recently described by Gooch and Eddy[2] which is almost identical with that devised in the present work.

One of the great advantages of this process is that the precipitation of calcium, strontium, and barium as carbonates is much more complete than in the usual method, where only a small quantity of ammonium carbonate is added, and where, to detect and remove these elements, it is necessary to add ammonium sulphate and ammonium oxalate to the filtrate. The process also makes unnecessary the lengthy operation of removing magnesium before testing for the alkali elements, which involves ignition to remove ammonium salts, precipitation of magnesium hydroxide by barium hydroxide, and subsequent removal of the barium. The only disadvantages of the process are that about half an hour is required to complete the precipitation of magnesium and that a somewhat longer time is required for filtration than when the carbonates are precipitated from a hot solution. These, however, seem slight in comparison with the lack of delicacy of the ordinary process of precipitation and the difficulty of subsequently removing magnesium.

In the analysis of the alkaline-earth group the ammonium carbonate precipitate is dissolved in acetic acid, and barium and strontium are precipitated as chromates, the former from an acetic acid solution of known concentration, the latter by making the filtrate alkaline with ammonia and adding alcohol. This method of precipitating barium

[1] Ann. Physik., **104**, 482 (1858).

[2] Am. J. Sci., [4], **25**, 444 (1908); Z. anorg. Chem., **59**, 427 (1908).

has been adopted in nearly all text-books in qualitative analysis, and the precipitation of strontium as chromate has been recommended by a few authors.[1] I was, however, found necessary to carry out a large number of experiments to determine the conditions under which a small amount of either element is easily detected and a large amount completely precipitated, and under which a large quantity of strontium, when present alone, does not interfere with the test for barium, and a large quantity of calcium does not interfere with that for strontium. This portion of the investigation was carried out by Dr. E. B. Spear in this laboratory.

After barium and strontium have been thus removed, calcium is precipitated as calcium oxalate, the filtrate is made strongly ammoniacal, and the magnesium precipitated by adding sodium phosphate and alcohol. In order to prevent the precipitation of some magnesium as oxalate when much of it is present, it is necessary to dilute the solution to about 300 ccm. before making the test for calcium; but this large volume does not prevent the detection of even less than 1 mgm. of magnesium. It may seem remarkable that the precipitation of magnesium ammonium phosphate is such a delicate test under these conditions, especially in view of the fact that it is usually directed to make the precipitation in as small a volume as possible. The difference is brought about by the presence in the solution of a moderate amount (about 20 per cent.) of alcohol, which doubtless greatly decreases the tendency of the solution to remain supersaturated.

The filtrate from the ammonium carbonate precipitate, which should now contain only salts of the alkali elements, is evaporated to dryness; the ammonium salts are expelled by ignition, and the residue dissolved in a little water. This solution is divided into two parts; the smaller one is tested for lithium and potassium, and the larger for sodium. Lithium is precipitated as phosphate from a hot, slightly alkaline solution, the delicacy of the test being greatly increased by the addition of a little alcohol. The potassium is tested for in the filtrate, after expelling the alcohol completely, by adding sodium cobaltinitrite, which gives a precipitate of $K_2NaCo(NO_2)_6H_2O$. This reaction has been used as a quantitative method of determining potassium;[2] it is delicate

[1] W. Fresenius and F. Ruppert, Z. analyt. Chem., **30**, 677 (1891). Caron and Raquet, Bull. soc. chim. [3], **35**, 1061 (1906).

[2] Adie and Wood, J. Chem. Soc., **77**, 1076 (1900). Drushel, Am. J. Sci. [4], **24**, 433 (1907); **26**, 329 (1908).

enough to enable 0.2–0.3 mgm. of potassium to be detected in 5 ccm. of solution. In order to detect sodium the second portion of solution is evaporated and treated with an alkaline potassium pyroantimonate solution.[1] When the reagent is properly prepared this test is satisfactory and reliable on account of the characteristic appearance of the crystals of sodium pyroantimonate formed, and it is delicate enough to detect 1 or 2 mgm. of sodium in the portion of solution tested. It is seldom that a more delicate test for this abundant element is necessary; indeed, if a much more sensitive one be employed, the sodium introduced in the process of analyses from the reagents, the glass vessels, and the dust of the air would prevent a blank being obtained in the absence of this element. For this reason, and because it gives no idea of the quantity present, the flame test relied upon in some schemes of analyses is unsatisfactory. Unfortunately, however, the presence of a large amount of a potassium salt prevents the precipitation of even several milligrams of sodium; moreover, even a small amount of lithium gives a similar precipitate. In these cases, before making the test for sodium, the lithium is removed by precipitating it as fluoride, and the potassium is greatly reduced in quantity by precipitating a large part of it as sulphate.

An as yet unpublished scheme of analysis for the alkali elements, which included also rubidium and cæsium, was worked out a few years ago in this laboratory by A. A. Noyes and J. E. Ober. In the first step of the process, following the method in common use, sufficient chlorplatinic acid was added to convert all the elements into the corresponding chlorplatinates; the sodium and lithium salts were washed out by means of alcohol, and the potassium, rubidium, and cæsium salts left undissolved. In the present scheme, in which the detection of the common elements is of primary importance, this process has not been adopted on account of the time required to make this separation and to remove the platinum before testing for sodium and lithium, and also on account of the expense involved in the use of the large amount of chlorplatinic acid required.

A final confirmatory test is given for each element except magnesium. These tests will be omitted by the experienced analyst except when a small precipitate or one of doubtful character is obtained. The test for calcium is made by treating the oxalate precipitate with dilute

[1] Cf. Boettger, Qualitative Analyse, Zweite Auflage, 232.

sulphuric acid, and precipitating the calcium sulphate from the solution by the addition of alcohol. The test for strontium depends on the transformation of the strontium chromate into carbonate at 100° in a solution containing sodium carbonate and sufficient oxalate to transform any calcium salt present into oxalate; the strontium is dissolved in acetic acid and precipitated by adding ammonium hydroxide and carbonate, and boiling. The presence of the remaining elements is confirmed by the usual flame tests. The confirmatory tests for calcium, strontium, barium, and lithium can be made in a still more satisfactory manner by the use of a small "pocket" spectroscope, comparative experiments being made with known solutions. A small instrument of this kind, which costs less than a platinum dish, should be available in every laboratory of qualitative analysis because of the educational value to the student.

Tabular Outline

In Table X an outline of the process is given, the confirmatory tests being, however, omitted. The symbols of the anhydrous substances are given without reference to the actual state of hydration of the precipitates. When lithium is not to be tested for, the directions enclosed within brackets are to be omitted. No attempt should be made to carry out an analysis without consulting the detailed directions given in the Procedures.

TABLE X — ANALYSIS OF THE ALKALINE-EARTH AND ALKALI GROUPS

Solution containing Ba, Sr, Ca, Mg; Li, K, Na.

Evaporate to a small volume, add $(NH_4)_2CO_3$ and alcohol, filter after ½ hour (P. 81).

<table>
<tr><td colspan="4">Precipitate: $BaCO_3$, $SrCO_3$, $CaCO_3$, $MgCO_3.(NH_4)_2CO_3$.
Dissolve in acetic acid, add K_2CrO_4 (P. 82).</td><td colspan="3">Filtrate. *Evaporate, ignite, add 5–10 ccm. water (P. 91).*</td></tr>
<tr><td rowspan="4">Precipitate:
$BaCrO_4$.</td><td colspan="3" rowspan="2">Filtrate. *Add NH_4OH and alcohol (P. 84).*</td><td colspan="2">*To one-third of solution [add NaOH and Na_2HPO_4, heat, add alcohol (*P. 91a)].*</td><td rowspan="2">Remainder. [*Precipitate Li as LiF (P. 94)*].
Evaporate to 1 ccm., add $K_2H_2Sb_2O_7$ reagent (P. 94).</td></tr>
<tr><td rowspan="3">Precipitate:
$SrCrO_4$.</td><td colspan="2" rowspan="2">Filtrate. *Dilute, add $(NH_4)_2C_2O_4$ (P. 86).*</td><td rowspan="3">Precipitate:
Li_3PO_4.</td><td rowspan="2">Solution.
Add $Na_3Co(NO_2)_6$ (P. 92).</td></tr>
<tr><td rowspan="2">Precipitate:
CaC_2O_4.</td><td rowspan="2">Filtrate.
Add NH_4OH and Na_2HPO_4 (P. 88).</td><td rowspan="2">White crystalline precipitate:
$Na_2H_2Sb_2O_7$.</td></tr>
<tr><td>Precipitate:
$MgNH_4PO_4$.</td><td>Precipitate:
$K_2NaCo(NO_2)_6$.</td></tr>
</table>

Procedures and Notes

Alkaline-Earth Group

Procedure 81. — Evaporate the filtrate from the NH_4OH and $(NH_4)_2S$ precipitate (P. 51) to a volume of about 10 ccm., and filter off any sulphur that may have precipitated. To the cold solution add 30 ccm. of the $(NH_4)_2CO_3$ reagent (see N. 2) and 30 ccm. 95% alcohol; let the mixture stand for at least half an hour, shaking frequently. (Precipitate, presence of ALKALINE-EARTH ELEMENTS.) Filter and wash the precipitate with a little of the $(NH_4)_2CO_3$ reagent; if the precipitate is large, dry it by suction. (Precipitate, P. 82; filtrate, P. 91.)

Notes.—1. The filtrate from the $(NH_4)_2S$ precipitate should be colorless or light yellow (see P. 51, N. 12). It is evaporated in order that the elements of the alkaline-earth group may be precipitated more quickly and more completely. The volume to which the $(NH_4)_2CO_3$ reagent is added should not exceed 20 ccm. The evaporation also serves to destroy $(NH_4)_2S$ and to coagulate any sulphur that may separate.

2. The reagent used in precipitating the elements of this group is conveniently prepared by dissolving 100 grams freshly powdered ammonium carbonate in 300 ccm. NH_4OH (0.96), filtering if there is any precipitate, and adding 100 ccm. NH_4OH (0.90). The solid carbonate contains a large proportion of ammonium carbamate, $NH_2CO_2NH_4$; but, on dissolving, the latter is rapidly converted into ammonium carbonate.

3. In an ammoniacal ammonium carbonate solution, calcium, strontium, and barium are precipitated as carbonates. If the ammonium carbonate and hydroxide were added in only small excess, the precipitation would not be complete, and additional tests for these elements would have to be made (for example, by adding to the filtrate $(NH_4)_2C_2O_4$ and $(NH_4)_2SO_4$). But by the use of a concentrated solution of $(NH_4)_2CO_3$, and the addition of a large excess of NH_4OH to diminish the hydrolysis of the carbonate into $(NH_4)^+HCO_3^-$ and NH_4OH, the precipitation may be made practically complete, owing to the greatly increased concentration of the carbonate ion (CO_3^{--}).

4. When the concentrations of $(NH_4)_2CO_3$ and NH_4OH are sufficiently great, magnesium is in the cold also quantitatively precipitated as a double carbonate, $MgCO_3.(NH_4)_2CO_3.4H_2O$. This substance is, however, fairly soluble in water, and the solubility increases rapidly with the temperature.

5. In an aqueous solution in the cold, the precipitation of these ele-

ments takes place slowly, especially in the case of magnesium and calcium, but it is greatly accelerated by the addition of alcohol and by shaking. Under the conditions recommended in the procedure, not more than 0.1–0.3 mgm. of any of the four elements remains in solution after half an hour, and even 0.5 mgm. is easily detected within this time.

6. Li_2CO_3 is by far the least soluble carbonate of the alkali elements, but under the conditions of the procedure no precipitate is obtained, even when 150 mgm. of lithium are present. Larger amounts of lithium yield a precipitate; but this case will seldom, if ever, occur if the weight of the original substance taken for analysis did not exceed 1 gram. The presence of the alkali elements does not interfere in the analysis of the alkaline-earth group, and it is therefore not necessary to wash the $(NH_4)_2CO_3$ precipitate.

Procedure 82. — Dissolve the $(NH_4)_2CO_3$ precipitate (P. 81) by pouring repeatedly through the filter a portion of hot dilute acetic acid (10–25 ccm. 30% acid). Make the solution slightly alkaline with NH_4OH; add 30% acetic acid, drop by drop, until the solution after shaking is just acid to litmus, and then add 3 ccm. more. Dilute to 40 ccm., heat just to boiling in a flask; measure out 10 ccm. 20% K_2CrO_4 solution and add it a few drops at a time; if a precipitate forms, heat the mixture just to boiling and shake it after each addition; finally, heat the mixture at 90–100° for 1 or 2 minutes, shaking it frequently. Filter, even though the solution appears clear; remove the filtrate, and wash the precipitate thoroughly with cold water. (Pale yellow precipitate, presence of BARIUM.) (Precipitate, P. 83; filtrate, P. 84.)

Notes.—1. The solubility in water of the chromates of the alkaline-earth elements increases rapidly in the order, Ba, Sr, Ca, Mg. The difference in solubility of $BaCrO_4$ and $SrCrO_4$ is so great that under the conditions of the procedure 0.5 mgm. Ba can be detected, while even 400 mgm. Sr give no precipitate. The amount of K_2CrO_4 added is sufficient to precipitate completely more than 500 mgm. of barium.

2. Acetic acid is added to prevent the precipitation of $SrCrO_4$. By its action the concentration of the chromate-ion is reduced, owing to its conversion into hydrochromate-ion and bichromate-ion, according to the reactions:

$$2CrO_4^{--} + 2H^+ = 2HCrO_4^- = H_2O + Cr_2O_7^{--}.$$

The relative amounts of these two ions present in the acid solution

depend upon the dilution; in the fairly concentrated solution used in this procedure $Cr_2O_7^{--}$ predominates, but this would be reversed in a much more dilute solution. Since $HCrO_4^-$ is a weaker acid than acetic acid, the CrO_4^{--} concentration in the acid solution is very small. It is evident that the CrO_4^{--} concentration decreases as the H^+ concentration increases. For this reason the presence of excess of a strong acid (such as HCl or HNO_3 in the absence of acetate) prevents the precipitation of $BaCrO_4$; but owing to the fact that acetic acid is itself a weak acid, and that a large amount of acetate is present, the addition of a considerable excess of acetic acid has but little effect. The most satisfactory separation of barium and strontium is obtained when a small excess of acetic acid is present; 2 ccm. 30% acetic acid is nearly equivalent to 10 ccm. 20% K_2CrO_4 solution.

3. The K_2CrO_4 is added slowly to a hot solution; the mixture is shaken and heated in the neighborhood of 100° before filtering, since otherwise the precipitate is liable to pass through the filter. By this method of precipitation almost all the barium is precipitated before an excess of K_2CrO_4 is added; this is of special importance when much barium is present, since as much as 3 mgm. Sr may then be carried down completely if the K_2CrO_4 reagent is added quickly. If for any reason the filtrate is turbid after two or three filtrations, the precipitate ($BaCrO_4$) may be coagulated by boiling gently for 1 or 2 minutes. Vigorous or long-continued boiling is to be avoided, since, owing to loss of acetic acid, $SrCrO_4$ may then separate if much strontium is present. The presence of 1 mgm. or more of barium is indicated by a distinct turbidity or the formation of a precipitate; when the amount is smaller than 1 mgm. it is very difficult to distinguish the faint turbidity in the colored solution, and the pale yellow precipitate can be seen only after filtering and washing the K_2CrO_4 out of the filter. The precipitate must always be washed thoroughly, in order to remove strontium as completely as possible, which otherwise would obscure the confirmatory test for barium in P. 83.

Procedure 83. — To confirm the presence of barium dissolve the K_2CrO_4 precipitate (P. 82), or a portion of it, in HCl (1.12), and evaporate the solution to a few drops. Dip a clean platinum wire into the solution, and introduce the wire into a colorless flame. (Green flame, presence of BARIUM.)

Note. — HCl is used, instead of HNO_3, in dissolving the precipitate, because the flame test for barium is then somewhat more delicate, owing

to the greater volatility of the chloride. When the amount of barium is very small, only a momentary green color is seen as the yellow (sodium) color which first appears fades away. The presence of chromium does not interfere with the test.

Procedure 84. — To the filtrate (P. 82), after cooling it, add NH_4OH (0.90) slowly until the color of the solution changes from orange to yellow, and then 3 ccm. more. Dilute the solution to 60 ccm., and add slowly, with constant shaking, 50 ccm. 95% alcohol. (Pale yellow precipitate, presence of STRONTIUM.) Filter after several minutes, using suction if filtration is slow; but do not wash the precipitate. (To ensure the complete precipitation of strontium, when much strontium or barium has been found, add to the filtrate 5 ccm. 20% K_2CrO_4 solution and 10 ccm. alcohol; filter off any precipitate that separates, and reject it if a precipitate has already been obtained in this procedure.) (Precipitate, P. 85; filtrate, P. 86.)

Note.— Under the conditions of the procedure, 0.5 mgm. of strontium is detected almost at once, and a smaller amount on standing; while even 400–500 mgm. of calcium or magnesium give no precipitate. A moderate change in the conditions will not affect this result; but if the concentration of alcohol or K_2CrO_4 is much less than is recommended, the precipitation of strontium may be incomplete; while the addition of larger amounts of alcohol and K_2CrO_4 may cause the precipitation of chromate of calcium or magnesium if much of these elements is present, or of K_2CrO_4 itself, since the latter is not very soluble in alcohol. The confirmatory test should therefore be tried. The precipitate is not washed, because $SrCrO_4$ is a fairly soluble substance.

Procedure 85. — To confirm the presence of strontium, transfer the precipitate (P. 84) (or a portion of it if the precipitate is large), with the filter if necessary, to a casserole; add a mixture of 30–35 ccm. 3% $Na_2C_2O_4$, 2 ccm. 10% Na_2CO_3 (both measured out in graduates), and about 0.5 ccm. 20% K_2CrO_4; cover the casserole with a watch glass, heat to boiling, and boil gently for 3–5 minutes. Filter, wash the precipitate thoroughly with water, pour repeatedly through the filter about 5 ccm. of 5% acetic acid; add to this solution NH_4OH in excess and 3–5 ccm. of the $(NH_4)_2CO_3$ reagent; heat to boiling in a small flask and set aside for 5–10 minutes. (White precipitate, presence of STRONTIUM.)

Notes.—1. In a boiling solution containing oxalate and carbonate in the proportions recommended in the procedure, small quantities of calcium and strontium are converted in a few minutes almost quantitatively into oxalate and carbonate, respectively. At 100° the solubility-product of calcium oxalate is not more than 1.5 times as great as that of calcium carbonate, and therefore the carbonate will be converted into the oxalate when the ratio of the concentrations of $Na_2C_2O_4$ and Na_2CO_3 is greater than this amount. The ratio adopted in the procedure is about 4 to 1. In the case of strontium, however, the oxalate is so much more soluble than the carbonate that even when this ratio is as great as 8 to 1 no strontium oxalate is formed. To provide for the very rare case that barium is present, a small amount of K_2CrO_4 is added; the barium then remains as $BaCrO_4$, the yellow color of which is easily seen on the filter after washing out the K_2CrO_4. In this procedure it will usually be more convenient to prepare a special reagent by dissolving 30 grams $Na_2C_2O_4$, 6 grams Na_2CO_3, and about 3 grams K_2CrO_4, and diluting the mixture to 1 liter.

2. In the treatment with dilute acetic acid the strontium is dissolved, but not enough calcium to give a test with ammonium carbonate. If barium is present, a little $BaCrO_4$ dissolves, giving a yellow solution; it may, however, be easily removed by adding excess of K_2CrO_4 and boiling the acid solution (see P. 82).

3. In this procedure the presence of 0.5 mgm. of strontium may be detected, and a perfect blank is obtained even with 30 mgm. of calcium or magnesium. With larger amounts of calcium, however, a very small precipitate may be obtained with ammonium carbonate.

4. If a spectroscope is available, the presence of strontium in the precipitate obtained in P. 84 may be quickly detected, after dissolving the precipitate in a little nitric acid and evaporating the solution to a few drops. Comparative tests with pure strontium and calcium solutions should be made.

Procedure 86.—To the filtrate (P. 84) add 200 ccm. water; heat to boiling, and add slowly to the boiling solution 20–50 ccm. 4% $(NH_4)_2C_2O_4.H_2O$ solution; shake, and let the mixture stand for several minutes. (White precipitate, presence of CALCIUM.) Filter, and wash the precipitate once with water. (Precipitate, P. 87; filtrate, P. 88.)

Note.—The solution is heated to boiling, the ammonium oxalate is added slowly, and the mixture is allowed to stand a few minutes, since

otherwise the filtration is slow and calcium oxalate may pass through the filter. Moreover, since small amounts of calcium do not precipitate rapidly in the cold, 2 or 3 mgm. may escape detection if the mixture is not heated. Under the conditions of the procedure, *i. e.*, in a volume of about 300 ccm., 0.5 mgm. of calcium can be detected within 5 minutes, while 400 mgm. of magnesium give no precipitate. If, however, the volume of the solution is much less than 300 ccm. and much magnesium is present, some may precipitate, especially if the mixture be allowed to cool to room temperature.

Procedure 87. — Dissolve the $(NH_4)_2C_2O_4$ precipitate (P. 86), or a portion of it, in 5 ccm. cold, dilute H_2SO_4 (1.20); filter if necessary; add 10–15 ccm. 95% alcohol, and let the mixture stand for several minutes. (White precipitate, presence of CALCIUM.)

Notes.—1. $CaC_2O_4.H_2O$ is very difficultly soluble in water, but dissolves in dilute solutions of highly ionized acids, owing to the formation by metathesis of un-ionized $HC_2O_4^-$. $CaSO_4$ is somewhat soluble in dilute H_2SO_4, but is completely thrown out as a flocculent precipitate by the addition of 2 or 3 volumes of alcohol. 1 mgm. of calcium gives a distinct turbidity at once, 0.5 mgm. in 1–3 minutes, and 0.2 mgm. within 10 minutes.

2. Moderate amounts of magnesium and of K_2CrO_4 do not interfere with this test, and it is therefore unnecessary to wash the precipitate thoroughly in P. 86. If strontium is present, however, a small amount of it dissolves in the H_2SO_4 and gives a slight turbidity at once on the addition of alcohol, corresponding to that given by only 0.2–0.3 mgm. of calcium after standing a few minutes. Therefore anything more than a slight turbidity is a conclusive proof of the presence of calcium.

Procedure 88. — To the filtrate from the $(NH_4)_2C_2O_4$ precipitate (P. 86) add 10 ccm. NH_4OH (0.90) and 20 ccm. 10% $Na_2HPO_4.12H_2O$ solution; cool, and shake the mixture; if no precipitate forms, let the mixture stand for at least half an hour, shaking it frequently. (White precipitate, presence of MAGNESIUM.)

Note.—This test for magnesium depends upon the precipitation of magnesium ammonium phosphate, $Mg^{++}(NH_4)^+PO_4^{---}$. This salt is somewhat soluble in water, owing chiefly to hydrolysis into NH_4OH and $Mg^{++}HPO_4^{--}$; and the test is therefore made in a strongly ammoniacal solution. Since the solubility increases rapidly with the temperature,

the solution is cooled to the room temperature, or below. In an aqueous solution this substance shows a great tendency to form a supersaturated solution, and it is therefore usually directed to make the test in as small a volume as possible. In the presence of alcohol, however, precipitation takes place rapidly, and even 0.5 mgm. of magnesium will give a distinct turbidity in this solution (containing 250 ccm. water and 50 ccm. alcohol) within half an hour, and the precipitate settles out on further standing. The presence of a small precipitate may then be detected by rotating the solution so as to cause the precipitate to collect in the centre. If calcium is present in this procedure, even as small an amount as 3 mgm. will give a distinct precipitate of calcium phosphate; it is therefore very important to precipitate the calcium completely as oxide in P. 86.

Analysis of the Alkali Group

Procedure 91. — Evaporate the filtrate from the $(NH_4)_2CO_3$ precipitate (P. 81) almost to dryness in a casserole; acidify with HCl; evaporate to dryness, and ignite the residue gently to a temperature below dull redness until no more white fumes come off, taking care to heat the sides as well as the bottom of the dish. Add about 10 ccm. water, warm, filter, evaporate the filtrate to dryness, and ignite again (to ensure complete removal of the ammonium salts). Add 5–10 ccm. water, and if necessary filter through a small filter. Test about one-third of the filtrate [first for lithium by *P. 91*a* and then] for potassium by P. 92; test the remainder of the filtrate for sodium by P. 93–94.

Notes.— 1. Great care must be taken to remove the ammonium salts completely, since the presence of even 1–2 mgm. of an ammonium salt would show the same reaction as potassium. The residue must not, however, be heated to redness, since the alkali elements might then be lost by the volatilization of their chlorides.

2. A brown or black residue of organic matter, coming from impurity in the ammonium salts used in the course of analysis and from the alcohol and filter paper, usually remains upon treating the ignited residue with water. Sometimes, owing to the presence of this organic matter, the aqueous solution after the first ignition has a dark or yellow color, but it is usually clear after the residue is heated a second time.

3. The larger portion of the solution is used for the detection of sodium, since the test for this element is less delicate than the tests for lithium and potassium.

***Procedure 91a.** — If lithium is to be tested for, evaporate one-third of the aqueous solution (P. 91) to 2 or 3 ccm. Pour it into a large test tube or small flask; add 0.3–0.5 ccm. 10% NaOH solution, and filter if there is a precipitate. Add 1–2 ccm. 10% $Na_2HPO_4.12H_2O$ solution, heat to boiling, add 1 ccm. alcohol, shake, and boil gently for about half a minute; add another portion of alcohol, and boil again for a few seconds. (White precipitate, presence of LITHIUM.) Filter, remove the filtrate, and wash the precipitate thoroughly with NH_4OH (0.96).

Dissolve the precipitate in dilute HCl, evaporate the solution to a few drops, dip the loop of a clean platinum wire into it, and introduce the loop into a colorless gas flame. (Brilliant red flame, presence of LITHIUM.)

To the filtrate from the Na_2HPO_4 precipitate add acetic acid until it is slightly acid, evaporate the solution to a few drops, and add 3–5 ccm. in water. Test the solution for potassium by P. 92.

Notes.—1. If magnesium was not completely removed in the $(NH_4)_2CO_3$ treatment, it precipitates upon the addition of NaOH; it should be filtered off, since otherwise it would be converted into phosphate and be mistaken for lithium.

2. Li_3PO_4 is difficultly soluble in both hot and cold water; but the solubility is still less in an alkaline solution, since its hydrolysis into $(Li^+)_2HPO_4^{--}$ and Li^+OH^- is then diminished. The presence of NaOH is, moreover, necessary, in order to neutralize the acid formed in the reaction between the lithium salt and Na_2HPO_4. The tendency of Li_3PO_4 to form a supersaturated solution is overcome by heating the mixture, and by the addition of alcohol. Under the conditions of the procedure, 0.3 mgm. Li may be easily detected in the portion of solution used, and even 0.2 mgm. when the second portion of alcohol is added and the mixture again boiled.

3. The alcohol is expelled before testing the filtrate for potassium, because the presence of both alcohol and Na_2HPO_4 in a $Na_3Co(NO_2)_6$ solution causes the formation of a violet precipitate on standing. If a precipitate of Li_3PO_4 is formed by Na_2HPO_4 alone, the addition of alcohol and the subsequent evaporation are unnecessary.

4. Before making the confirmatory test, it is important to wash out the sodium salts as far as possible, otherwise the yellow color of the sodium flame may completely obscure the red color due to lithium. When the amount of lithium present is very small (0.2–0.3 mgm.),

there will always be enough sodium present to cause the flame of lithium to appear of a reddish yellow, instead of brilliant red color.

5. If a small spectroscope is available, time can often be saved by examining with it the solution before the addition of NaOH and Na_2HPO_4; for if the characteristic red line of lithium is absent, this procedure may be omitted. If present, this procedure will serve to give an estimate of its quantity, which can hardly be formed from an ordinary spectroscopic examination.

Procedure 92. — To one-third of the solution (P. 91) [or to the filtrate from the Na_2HPO_4 precipitate (*P. 91*a*)], whose volume should not exceed 5 ccm., add a few drops of acetic acid, if the solution is not already acid, and an equal volume of $Na_3Co(NO_2)_6$ reagent. If no precipitate forms at once, let the mixture stand for at least 15 minutes. Filter, and wash the precipitate thoroughly with water. (Yellow precipitate, presence of POTASSIUM.)

Dissolve the precipitate, or a portion of it, in hot dilute HCl, evaporate to a few drops, dip a clean platinum wire into the solution, and introduce it into a colorless gas flame, viewing the flame through a sufficient thickness of blue cobalt glass to cut off sodium light. (Violet flame, presence of POTASSIUM.)

Notes. — 1. To prepare the solution of sodium cobaltinitrite, $Na_3Co(NO_2)_6$, used as a reagent, dissolve 100 grams $NaNO_2$ in about 200 ccm. water, add 60 ccm. 30% acetic acid and 10 grams $Co(NO_3)_2.6H_2O$; let the mixture stand for a day or two, filter off any precipitate that is formed (such as $K_2NaCo(NO_2)_6.H_2O$, arising from the presence of potassium as an impurity in the reagents), and dilute the solution to 400 ccm. For the chemical reactions involved, see Part III, P. 69, N. 1.

2. The presence of 0.3 mgm. of potassium in 5 ccm. of solution may be easily detected within 5 or 10 minutes, and an even smaller amount on long standing. The yellow color of the precipitate is best seen on the filter after washing out the $Na_3Co(NO_2)_6$ thoroughly. The solution must not be alkaline when the $Na_3Co(NO_2)_6$ reagent is added, since $Co(OH)_3$ would then be precipitated. In the presence of an ammonium salt (containing even 0.5–1.0 mgm. NH_4) a precipitate is obtained very similar in appearance to that obtained with potassium; but moderate amounts of the alkaline-earth elements or of lithium do not interfere with the test.

3. The flame test for sodium is so much more delicate than that for potassium that the yellow color due to a trace of sodium may completely

obscure the color given by a moderate amount of potassium. A sufficient thickness of cobalt blue glass is used to absorb the yellow rays completely, and thus permit the violet rays due to potassium to be seen. Comparative experiments with known solutions ought always to be made, unless the analyst is perfectly familiar with the appearance of the flames. If a spectroscope is used, the characteristic potassium line will be found near the red end of the spectrum.

Procedure 93. — In the absence of lithium (*P. 91*a*) or of much potassium (P. 92), test the remainder of the solution (P. 91) for sodium by P. 94.

If much potassium was found (and no lithium), add about 1 ccm. H_2SO_4 (1.84), evaporate in a casserole, and heat strongly until the white fumes cease to come off; let the mixture cool; add a few drops of water and 10% KOH solution until the solution is alkaline. Evaporate to about 2 ccm., cool, filter or decant off the solution, wash the crystals with a few drops of water, and test the solution for sodium by P. 94.

*If lithium is present, evaporate the solution to 2 ccm. (or 5 ccm. if much lithium is present); add 1 ccm. NH_4OH (0.90) and 2–4 ccm. 20% NH_4F solution; shake, and filter after a few minutes. To the filtrate add HCl, evaporate to dryness (in a platinum dish under a hood), heat to expel ammonium salts, add HCl, and evaporate to dryness. Dissolve in a little water, and treat the solution by P. 94, or by the preceding paragraph if much potassium is present.

Notes.— 1. The presence of a large amount of potassium salt, as KCl or KNO_3, in P. 94 greatly decreases the delicacy of the test for sodium. The process here recommended for the removal of a large part of the potassium depends on the relatively slight solubility of K_2SO_4 (as compared with KCl or KNO_3), and on the fact that the saturated solution may be easily separated from the heavy crystals of K_2SO_4 either by decantation or by filtering through a small filter. In the presence of 300 mgm. potassium as chloride, 7 mgm. of sodium may escape detection if the mixture is treated directly by P. 94, but the present process enables 2–3 mgm. to be found. Unless the solution contains more than 50–100 mgm. potassium, this treatment is unnecessary.

*2. Since even 2 mgm. of lithium will interfere with the test for sodium in P. 94, the lithium must be removed before making this test. The precipitation as LiF is not complete; but, if the directions are followed, the filtrate will not contain more than 1 mgm. of lithium. The

process will not be satisfactory if the volume of the solution is too large or if too little NH_4F is used. If much sodium is present, some NaF will also be precipitated; but the filtrate will contain 50–100 mgm. of sodium if the volume is not less than 5 ccm.

*3. As an alternative process for the separation of the alkali elements, the lithium may be first precipitated as fluoride, and potassium and sodium tested for in separate portions of the filtrate. In this case, owing to the precipitation of NaF when much is present, it is always necessary to test for lithium in the NH_4F precipitate, which may be done by dissolving it in HCl, evaporating in a platinum dish, dissolving, and treating with Na_2HPO_4 by *P. 91a. When LiF is precipitated as directed in the present procedure, it is just possible to detect and confirm 1 mgm. Li. If the volume is decreased in order to obtain a more delicate test, the amount of sodium that remains in solution is also greatly decreased. This alternative process has therefore no advantages over the one adopted.

*4. When only chlorides are present, lithium may be conveniently separated from sodium (and potassium) by extracting the dry chlorides with 5–10 ccm. of a mixture of equal volumes of absolute alcohol and ether, in which LiCl alone dissolves; but the method is not applicable in all cases; for example, when sulphates are present.

Procedure 94. — If the solution that is to be tested for sodium (P. 93) reacts acid with litmus paper, add 10% KOH solution, drop by drop, until it is neutral or slightly alkaline. Evaporate the solution to about 1 ccm. and cool it. Add 1–2 ccm. $K_2H_2Sb_2O_7$ reagent; pour the mixture at once into a test tube, and let it stand for at least half an hour, or, better, over night. (White crystalline precipitate, presence of SODIUM.)

Decant off the solution, wash the precipitate several times with water, and dissolve it in a little HCl. Evaporate the solution to a few drops, and introduce a little of it on a platinum wire into a colorless gas flame. (Brilliant yellow flame, presence of SODIUM.)

Notes.—1. The dipotassium dihydrogen pyroantimonate ($K_2H_2Sb_2O_7$) reagent is prepared as follows: Add 2 grams of the best commercial salt to 100 ccm. boiling water, boil for about 1 minute until nearly all the salt is dissolved, quickly cool the solution, add about 3 ccm. 10% KOH solution, and filter. If a (flocculent) precipitate settles out on standing, decant off the clear solution. This reagent will usually keep for several months, but it should be tested frequently with a known solution of a

pure sodium salt. When a pyroantimonate solution is made slightly acid, it decomposes rapidly with precipitation of metantimonic acid. The same reaction takes place slowly in neutral solutions, owing to hydrolysis.

2. In this test with the antimonate, if 2 ccm. of the reagent are added to 1 ccm. of solution, 2 mgm. Na should give a distinct crystalline precipitate in less than 5 minutes, 1 mgm. within 30 minutes, and a smaller amount on standing several hours. The precipitate is a heavy crystalline, granular one, and usually adheres in part to the glass, where it can best be seen by tilting the test tube. Although in a solution of a pure sodium salt 1 mgm. of sodium is easily detected, yet in an actual analysis, owing to the presence of potassium salt and of certain substances that obscure the test, it is often difficult to detect less than 2 or 3 mgm. Thus a distinct turbidity is produced by even 0.1–0.2 mgm. of calcium barium or magnesium, and by 1–2 mgm. of aluminum. These light, flocculent precipitates are, however, very different from the heavy crystalline precipitate obtained with sodium, especially if the mixture has been allowed to stand a few hours. These crystals may be separated from a flocculent precipitate by shaking the mixture, waiting long enough for the heavy crystals to settle and decanting off the suspended, flocculent precipitate.

3. In the flame test the yellow color is to be regarded as a confirmation of the presence of an appreciable amount of sodium in the sample only when a brilliant, large, spreading flame is obtained. Owing to the delicacy of the test, there is always sufficient sodium present to give a slight yellow color. The chief value of this test is in proving the absence of lithium, since the precipitate due to lithium is very similar in appearance to sodium pyroantimonate.

Test Analyses

The following analyses were made to test the efficiency of the process. Nos. 184, 185, 187, 189, 193, 195 were made by Mr. A. B. Babcock, almost all of them as unknowns.

Analyses 182–205 were begun at P. 81.

T. A. No.	182	183	184	185	186–187	188–189
Ba	500 S	500 S	500 S	500 S	500 S	500 S
Sr	0 S	1 F[1]	3 F[1]	5 S—[1]	1 S	0 S
Ca	0 S[2]	1 S	. .	. .	. .	. .
Mg	0 S	1 S	. .	. .	. .	. .

T. A. No.	190	191	192	193	194–195	196
Ba	1 S	0 S	0 S	1 S	0 S	1 S
Sr	400 S	400 S	0 S	0 F[3]	0 S	1 S
Ca	0 S[2]	1 S	500 S	500 S	0 S[2]	1 S
Mg	0 S	1 S	0 S	1 S	400 S	400 S

T. A. No.	197	198	199	200–201	202	203	204	205
Sr	. .	. .	. .	. .	. .	. .	200—	200—
Mg	400—	400—	400—	5—	5—	5—	. .	. .
Li	0 S	1 S—[6]	1 S—[6]	. .	. .	. .	0 S	1 S
K	0 S	1 F[5]	1 S—	0 S	2 S	1 S	0 S	1 S
Na	0 S[4]	2 F[5]	2 D	0 S[4]	4 S	2 S[7]	0 S	2 F[5]

Analyses 206–213 were begun at *P. 91*a*. In each case the whole solution was used in making each test, instead of only one-third as directed in P. 91.

T. A. No.	206	207	208	209	210	211	212	213
Li	0 S	0 S	1 S	0.3 S[9]	0 S	0.3 S[9]	100 S	100 S
K	0 S[8]	0.5 S	0 S[8]	. .	170 S	170—	0 S	0.5 S
Na	300—	300—	200—	300—	. .	. .	. .	. .

Analyses 214–221 were begun at P. 93. The whole solution was used in testing for sodium, instead of two-thirds as directed in P. 91.

T. A. No.	214	215	216	217	218	219	220	221
Li	. .	. .	. .	. .	. .	100 —	100 —	100 —
K	300 —	300 —	200 —	300 —	300 —	. .	. .	. .
Na	0 S	3 S	2 S[7]	2 F	1 F	0 S	2 S	1 F

NOTES

[1] In Analyses 183–185 strontium was carried down with $BaCrO_4$ in P. 82 because the K_2CrO_4 reagent was added all at once in precipitating $BaCrO_4$, instead of slowly as directed.

[2] In testing for calcium in T. A. 182, 190, 194, and 195, very small precipitates were obtained, which were estimated to contain only 0.1–0.2 mgm. Ca. The precipitates obtained in T. A. 183, 191, and 196 when 1 mgm. Ca was present were much larger.

[3] In T. A. 193 several mgm. Ca were precipitated as chromate in P. 84, probably because a little too much alcohol was added. The precipitate was filtered off and dissolved in HNO_3; 10 ccm. 30% acetic acid were added, and NH_4OH to precipitate $Cr(OH)_3$; P. 84 was repeated. Less than 0.5 mgm. Sr was found, which was present as impurity in the calcium salt. The calcium used in T. A. 192 was first freed from strontium by means of P. 84.

[4] In the tests for sodium in T. A. 197 and 200, small flocculent precipitates were obtained corresponding to 0.2–0.3 mgm. Mg. In T. A. 201 a perfect blank was obtained.

[5] The $Na_3Co(NO_2)_6$ reagent used in testing for K in T. A. 198, and the $K_2H_2Sb_2O_7$ reagent used in testing for sodium in T. A. 198 (and possibly 205), were not properly made and were not used in the other experiments.

[6] In T. A. 198 and 199 lithium was confirmed by means of a small spectroscope.

[7] The sodium tests in T. A. 203 and 216 were distinct after standing several hours.

[8] In T. A. 206 and 208 small precipitates corresponding to 0.1–0.2 mgm. K separated, owing to presence of potassium in the NaOH reagent used in *P. 91*a*.

[9] In T. A. 209 and 211 the precipitate of Li_3PO_4 did not form until the second portion of alcohol was added and the solution boiled, but the precipitate was then very distinct.

These analyses, together with the experiments on the delicacy of the separate tests, show that 1 mgm. of each element except sodium can be detected in any combination; also that 2 mgm. of sodium (in the sample) can be found in simple combinations, and 3 mgm. in every case except in the presence of a very large amount of potassium (T. A. 217).

CONFIRMATORY EXPERIMENTS AND REFERENCES

P. 81, N. 3-5: *Precipitation of Alkaline-Earth Elements by Ammonium Carbonate.* — For the precipitation of $MgCO_3.(NH_4)_2CO_3.4H_2O$, see Gooch and Eddy, *Am. J. Sci.* [4] **25**, 444 (1908); *Z. anorg. Chem.*, **59**, 427 (1908).

Varying small amounts of Ca, Sr, Ba and Mg as nitrates, in separate experiments, were dissolved in 4 ccm. HCl (1.12); the solutions were neutralized with NH_4OH and diluted (or evaporated) to 10 ccm.; 30 ccm. of the $(NH_4)_2CO_3$ reagent (Note 2) and finally 30 ccm. alcohol were added; the mixtures were shaken frequently and examined at intervals, with the following results:

0.5 mgm.	Ca.	Sr.	Ba.	Mg.
Solution distinctly turbid in	5	5	5–10	15–20 minutes
Very distinct test in	10	15–20	20–30	30 minutes

With 1 mgm. the same results were obtained more quickly in each case; with 2 mgm. a distinct test was obtained in less than 5 minutes in each case. Even with 0.3 mgm. Mg a better test was obtained in half an hour than in a blank experiment (with no magnesium) over night.

The above experiments were repeated with 500 mgm. of each element; the precipitates were thick and gelatinous, but soon became more crystalline when the mixtures were shaken. The precipitates were filtered off after half an hour, and the filtrates allowed to stand: no precipitate separated in any case. Each filtrate was finally evaporated almost to dryness and tested, — in the case of calcium, with NH_4OH and $(NH_4)_2C_2O_4$, strontium and barium with H_2SO_4, and magnesium with NH_4OH, Na_2HPO_4, and alcohol: no calcium was found, less than 0.1 mgm. Ba or Mg, and less than 0.2 mgm. Sr. — The experiment with 500 mgm. Mg was repeated, except that the mixture was filtered after 15 minutes: a small precipitate separated in the filtrate on standing which was estimated to contain 1 to 2 mgm. Mg.

To determine the effect of shaking, the experiment with 500 mgm. Mg was repeated, except that the mixture was shaken only once at the beginning of the experiment; the mixture was filtered after half an hour, and the filtrate allowed to stand: a precipitate separated corresponding to 2 or 3 mgm. Mg. — It was also observed in the case of each element that the precipitates became crystalline more rapidly, and were much more easily filtered off if the mixtures were shaken frequently.

To determine the effect of the addition of alcohol, the experiment with

500 mgm. Mg was repeated several times, except that 10–20 ccm. alcohol were added instead of 30 ccm.: on filtering after half an hour and allowing the filtrates to stand over night, precipitates formed corresponding to several mgm. Mg, the amounts increasing rapidly as the amount of alcohol decreased. — The experiments with 0.5–2 mgm. of each element were repeated, except that no alcohol was added: with barium the precipitates formed as quickly as in the presence of alcohol, and with strontium almost as quickly; but in the experiments with 0.5 and 1.0 mgm. Ca or Mg no precipitates were obtained.

Experiments with 0.5 and 1.0 mgm. of each element to determine the effect of dilution showed that the solutions became turbid somewhat less quickly when the volume of the solution before adding the $(NH_4)_2CO_3$ reagent was 20 ccm. instead of 10 ccm. The difference was most marked in the case of magnesium, and 0.5 mgm. might easily escape detection if the volume were still greater.

A large number of experiments similar to those described above were performed with another $(NH_4)_2CO_3$ reagent containing in 30 ccm. about 5 grams ammonium carbonate and 20 ccm. NH_4OH (0.90), *i.e.*, less $(NH_4)_2CO_3$ and more NH_4OH than the regular reagent: the results were almost identical.

The following experiments were performed to determine the effect of heating. 20 mgm. Mg as $MgCl_2$ were dissolved in 4 ccm. HCl (1.12); the solution was neutralized with NH_4OH and diluted to 10 ccm.; 30 ccm. of a solution containing 10 ccm. NH_4OH (0.90) and 3 grams $(NH_4)_2CO_3$ were added: a large precipitate appeared quickly. After several minutes the mixture was heated gently: the precipitate dissolved and a clear solution resulted at 60–70°. The mixture was cooled rapidly to room temperature: a large precipitate separated, showing that the magnesium is much more completely precipitated at low temperatures. After half an hour the precipitate was filtered off, and Na_2HPO_4 and alcohol were added to the filtrate: a precipitate separated that was estimated to contain about 4 mgm. Mg. — In separate experiments 1 and 2 mgm. of Ca, Sr, and Ba as chlorides were dissolved in HCl (1.12); the solutions were neutralized with NH_4OH (0.90) and an excess of 10 ccm. added; the solutions were diluted to 40 ccm., 3 grams powdered $(NH_4)_2CO_3$ were added; the mixtures were heated just to boiling, and filtered after 10 minutes; the amount of unprecipitated metal in the filtrate was estimated as described above: in each case distinct precipitates of the carbonates were obtained which filtered readily, and the filtrates were estimated to contain less than 0.1 mgm. Ba, 0.2 mgm. Sr, and 0.1 mgm. Ca. — These experiments were repeated except that to 10 ccm. of each solution were added 30 ccm. of a solution containing 20 ccm. NH_4OH (0.90) and 5 grams $(NH_4)_2CO_3$; no alcohol was added, and the mixtures were boiled

vigorously in flasks for 1 minute: the results were almost the same as before. — The last experiment was repeated with 500 mgm. Ca and with 500 mgm. Ba: in each case the filtrate contained not more than 0.1 mgm. of the element, and the precipitate was more granular and more readily filtered than when the carbonate was precipitated in the cold in the presence of alcohol.

1 mgm. Ba as chloride was dissolved in 4 ccm. HCl (1.12), the solution was neutralized with NH_4OH (0.96), and an excess of 4 ccm. added; after dilution to 40 ccm. 3 grams powdered $(NH_4)_2CO_3$ were added, the mixture was heated to boiling and allowed to stand: the solutions remained clear for at least half an hour. — The experiment was repeated with 2 mgm. Ba: the solution remained clear for a minute or two after boiling, and then a very small precipitate formed. On standing for a day or two, however, nearly all the barium precipitated. These results, together with those in the preceding section, show that the precipitation of barium is greatly accelerated by the presence of a large excess of NH_4OH.

1, 2, 3, and 5 mgm. Mg as $MgCl_2$ were dissolved separately in 4 ccm. HCl (1.12); the solutions were neutralized with NH_4OH and diluted to 10 ccm.; 30 ccm. of a solution containing 10 ccm. NH_4OH (0.90) and 5 grams $(NH_4)_2CO_3$ were added; the mixtures were shaken frequently. The experiments were repeated with twice as much free NH_4OH in the same volume. The results showed that precipitates formed more quickly in the solutions containing more magnesium, but that there was very little difference between the two series of experiments. — In another series of experiments with much less NH_4OH, the magnesium precipitates formed much less rapidly. — In a series of experiments with 20 ccm. NH_4OH (0.90) and 3 grams $(NH_4)_2CO_3$ the precipitation of the magnesium took place much more slowly than in the experiments with 5 grams $(NH_4)_2CO_3$, and the filtrates after 16 hours contained 0.5–1.0 mgm. Mg instead of 0.1–0.2 mgm. Therefore the most favorable conditions for the complete and rapid precipitation of magnesium are to have the solution very concentrated with respect to both NH_4OH and $(NH_4)_2CO_3$. As shown above, the addition of alcohol enables 0.5 mgm. Mg to be detected in half an hour; but this result depends also upon the presence of large amounts of NH_4OH and of $(NH_4)_2CO_3$.

P. 81, N. 6: *Precipitation of Lithium by Ammonium Carbonate.* — 150 mgm. Li as chloride were treated by P. 81 exactly as described in the first experiments under N. 3 and 4 above: after half an hour the solution was perfectly clear and there was no precipitate; after 5 hours there was a precipitate, which, however, was smaller than that obtained with 0.5 mgm. magnesium. The experiment was repeated with 200 mgm. Li: a granular precipitate separated very slowly; it was very small in 30 minutes, but after 24 hours it was estimated to contain 20–40 mgm. Li.

Behavior of Lithium in the Analysis of the Alkaline-Earth Group. —

100 mgm. Li as LiCl were dissolved in acetic acid and treated by P. 82–88: no precipitate whatever was obtained in the procedures for the detection of Ba, Sr, and Mg, and only a very small one in that for the detection of Ca, which corresponded to 0.2–0.4 mgm. Ca, and was doubtless due to the presence of calcium as an impurity.

P. 82, N. 1–3: *Solubility of Barium and Strontium Chromates in Water.* — According to the conductivity measurements of Kohlrausch and Rose, *Z. physik. Chem.*, **12**, 241 (1893), the solubility of $BaCrO_4$ is 1.5×10^{-5} mols per liter at 18° and 2.0×10^{-5} at 25°. — Meschezerski, *Z. analyt. Chem.*, **21**, 399 (1882), found that its solubility at the boiling point of water is 1.7×10^{-4} mols per liter: also that in the precipitation of $BaCrO_4$ foreign substances are carried down with the precipitate. — R. Fresenius, *Z. analyt. Chem.*, **29**, 413–419 (1890), collected earlier data, and also showed experimentally that the solubility of $BaCrO_4$ is somewhat increased by ammonium salts and in a marked degree by acetic acid. He described a method of separating barium and strontium by precipitating $BaCrO_4$, but found that two precipitations were necessary in order to obtain the barium free from strontium.

R. Fresenius (*loc. cit.*, 419) determined the solubility of $SrCrO_4$ at 15° to be 5.9×10^{-3} mols per liter; he found that the presence of ammonium salts increased the solubility, but to a much less extent than dilute acetic acid.

The Precipitation of Barium as Chromate. — 0, 0.5, 1, and 2 mgm. Ba as nitrate were dissolved separately in 10 ccm. 30% acetic acid; the solutions were neutralized with NH_4OH, 3 ccm. acetic acid were added, and the mixtures were treated by P. 82: in the experiment with 2 mgm. the mixture became turbid at once on adding K_2CrO_4 to the hot solution; in the experiment with 1 mgm. the turbidity was less marked but was distinct; in the experiment with 0.5 mgm. the turbidity could hardly be distinguished at all, even by comparison with the solution obtained in the blank experiment. Each of the mixtures was filtered twice, and the precipitate was washed with cold water until the color of K_2CrO_4 in the filter had disappeared: the yellow residue was very distinct in the experiments with 1 and 2 mgm., and was small but distinct in the experiment with 0.5 mgm; no residue could be seen in the blank experiment. The precipitates were tested by P. 83; the green flame test was obtained in each case, but was not very brilliant in the experiment with 0.5 mgm.

The experiments with 0.5 and 1 mgm. Ba were repeated, except that the precipitates were washed with 50% alcohol: the amounts of $BaCrO_4$ left in the filter seemed to be no greater than on washing with water, and the flame tests were no better; there is, therefore, no object in using the alcohol-water mixture in washing.

500 mgm. Ba as nitrate were treated by P. 82: the large granular precipitate settled quickly, and the filtrate was clear after two filtrations. 5 ccm.

20% K_2CrO_4 solution were added to the filtrate, and the mixture was boiled for 2 or 3 minutes; no precipitate separated, showing that the precipitation of barium was complete.

500 mgm. Ba as nitrate were dissolved in 10 ccm. 30% acetic acid and treated by P. 82, except that the solution was not heated before adding K_2CrO_4, and the resulting mixture was not shaken: the large precipitate was very finely divided, did not settle quickly, filtered very slowly, and ran through the filter. The turbid filtrate was heated to boiling and boiled very gently for a minute or two: on filtering a clear solution resulted.

The Separation of Barium and Strontium. — 400 mgm. Sr as nitrate and a mixture of 400 mgm. Sr and 1 mgm. Ba as nitrates were dissolved separately in 10 ccm. 30% acetic acid, and treated by P. 82: with strontium alone a perfect blank was obtained in the K_2CrO_4 test for barium; while in the experiment with 1 mgm. Ba a distinct precipitate was obtained. In the latter case the confirmatory flame test showed the presence of a little strontium with the barium, but it was possible to distinguish the green color due to barium; the presence of barium was more easily proved by means of a small spectroscope.

To determine the effect of long-continued boiling the experiment with 400 mgm. Sr was repeated; the clear solution that resulted was boiled vigorously for 2 minutes: a granular precipitate of $SrCrO_4$ began to separate and increased somewhat on continued boiling. — The experiment was repeated with 200 mgm. Sr: no precipitate separated even on boiling for 10 minutes.

A mixture of 500 mgm. Ba and 1 mgm. Sr was dissolved in 10 ccm. 30% acetic acid and treated by P. 82; the first 2–3 ccm. K_2CrO_4 solution were added a few drops at a time, and the mixture was heated and shaken frequently; the remainder of the K_2CrO_4 solution was added quickly; the filtrate was tested for strontium by P. 84: a distinct precipitate of $SrCrO_4$ was obtained, which was estimated to contain at least 0.5 mgm. Sr. — The experiment was repeated with 500 mgm. Ba mixed with 1, 3, and 5 mgm. Sr, respectively, but the 10 ccm. portion of K_2CrO_4 solution was added all at once instead of very slowly: the $BaCrO_4$ ran through the filter in each experiment, and to obtain a clear filtrate it was necessary to filter several times through the same filter, or to boil the turbid filtrate for a minute or two. The clear filtrates were finally tested for strontium by P. 84: in each of several experiments with 1 mgm. Sr no precipitate of $SrCrO_4$ formed; in the experiments with 3 mgm. the $SrCrO_4$ precipitate was estimated to contain 0.1–0.5 mgm. Sr; and in the case of 5 mgm. the precipitate contained about 1.5 mgm. Sr. Therefore, if the K_2CrO_4 reagent is added quickly in precipitating barium, the $BaCrO_4$ precipitate runs through the filter, and as much as 3 mgm. Sr may be carried down almost completely by 500 mgm. Ba in P. 82.

Effect of Varying the Excess of Acetic Acid and of Chromate. — In each of a series of experiments 0.5 mgm. Ba as nitrate was dissolved in 10 ccm. 30% acetic acid and treated by P. 82 and 83, except that the excess of 30% acetic acid added to the neutral solution in P. 82 was varied: with 2 ccm. and 4 ccm. acetic acid the tests on the filter, after washing out the K_2CrO_4, were similar to that obtained with 3 ccm. acid, and the flame tests were distinct; with 6 ccm. acetic acid the yellow precipitate on the filter could scarcely be distinguished, but a small flame test was obtained; with a larger amount of acetic acid the tests failed. The experiments were repeated with 1 mgm. Ba: with 10 ccm. acetic acid faint tests for barium were obtained; with 15 ccm. the tests failed. — A few quantitative experiments were performed with acetic acid alone, without neutralizing with NH_4OH as in the preceding experiments: the precipitation of barium was quantitative with 2 or 3 ccm. acetic acid (*i. e.*, with the amount equivalent to the K_2CrO_4 present), but the solubility of $BaCrO_4$ increased rapidly when more acetic acid was used.

The above series of experiments with 1 mgm. Ba was repeated, except that 5 ccm. 20% K_2CrO_4 (instead of 10 ccm.) were used: distinct tests for barium were obtained when 3 ccm. acetic acid were added after neutralization, but the precipitation was not quite complete; the tests were very poor with 5 ccm. excess acetic acid, and failed with 6 ccm., showing that the precipitation is less complete and that acetic acid has a greater influence when the amount of chromate is decreased.

200 mgm. Sr as nitrate and 10 ccm. 30% acetic acid were treated by P. 82, except that only 1 ccm. acetic acid was added after neutralizing with NH_4OH: a precipitate of $SrCrO_4$ separated, corresponding to about 20 mgm. Sr. — The experiment was repeated with 400 mgm. Sr: a very large precipitate separated. 400 mgm. Sr as nitrate and 10 ccm. 30% acetic acid were treated by P. 82, except that an excess of only 2 ccm. acetic acid was added: a precipitate of $SrCrO_4$ separated which was estimated to contain about 10 mgm. Sr. — The experiments with 400 mgm. Sr were repeated with 3 and with 4 ccm. excess acetic acid: no precipitate separated in either experiment (except on boiling the solutions for a minute or two). Therefore strontium, when present alone, will precipitate in this procedure if too little acetic acid is added.

State of Chromic Acid in Solution. — See Sherrill, *J. Am. Chem. Soc.*, **29**, 1641 (1907).

P. 83, N. 1: *The Flame Test for Barium.* — Compare C. E. on P. 82. 0.5 mgm. Ba as chloride was tested by P. 83: a distinct green flame was obtained. — The experiment was repeated, the barium being first precipitated as $BaCrO_4$ in P. 82: the first flash on introducing the wire into the flame was yellow, but the green color appeared for a moment as this color died

away. — The experiment was repeated in the presence of several milligrams of chromium as $CrCl_3$ and as $Cr(NO_3)_3$: the result was the same. No green flame was obtained with chromium salts alone.

1.0 mgm. Ba was precipitated in P. 82 as chromate; the precipitate was washed and dissolved in HNO_3; the solution was evaporated to 2 or 3 drops and the yellow solution was tested by P. 83: a faint green color was seen as the yellow flame died away. Excess of HCl was then added, and the mixture evaporated to a few drops: the yellow color of the solution changed to green, owing to reduction of chromate; the flame test for barium was more distinct than in the presence of HNO_3. This experiment was repeated several times, always with the same result.

P. 84, N. 1: *Solubility of $SrCrO_4$, $CaCrO_4$, and $MgCrO_4$ in Water and in Mixtures of Alcohol and Water.* — W. Fresenius and F. Ruppert, *Z. analyt. Chem.*, **30**, 677 (1891), found the solubility of $SrCrO_4$ in 29 antl 53 volume per cent. alcohol at room temperature to be 6.5×10^{-4} and 1.0×10^{-4} mols per liter. The solubility of calcium chromate in 29 and 53 volume per cent. alcohol was found to be 7.8×10^{-2} and 5.6×10^{-2} mols per liter.

Mylius and Wrachem (*cf.* Seidell, *Solubilities*, **90**) prepared several different chromates, $CaCrO_4$, $CaCrO_4.\frac{1}{2}H_2O$, $CaCrO_4.H_2O$, $\alpha CaCrO_4.2H_2O$, and $\beta CaCrO_4.2H_2O$; and found their solubilities in water to increase in the order given, and to decrease with rising temperature. Since the solubility of $SrCrO_4$ increases with rising temperature, the separation of calcium and strontium will be more satisfactory at room temperature, as recommended in P. 84, than at 70°, as recommended by W. Fresenius and F. Ruppert. We have found that a precipitate sometimes separates in P. 84 when a very large amount of calcium is present, and increases in amount on standing; this indicates that the solution first obtained was supersaturated with respect to one or more of these chromates.

According to Mylius and Funk, *Ber.*, **30**, 1718 (1897), the solubility of $MgCrO_4.7H_2O$ at 18° is 42.0 grams $MgCrO_4$ in 100 grams of solution (sp. gr. 1.422). Schweitzer (*cf.* Seidell, *Solubilities*, **181**) found the solubility of the double salt, $MgCrO_4.K_2CrO_4.2H_2O$, to be 28.2 grams in 100 grams water at 20°, which seems to indicate that the double salt is more likely to separate in P. 84 than is $MgCrO_4.7H_2O$.

Separation of $SrCrO_4$ and $CaCrO_4$ by Means of Chromate and Alcohol. — W. Fresenius and F. Ruppert determined the difference in solubility of $SrCrO_4$ and $CaCrO_4$ in water and on adding alcohol (see preceding section), and first suggested a method based on it for use in qualitative analysis: they add K_2CrO_4 to a fairly dilute solution of the chlorides, free from HCl, heat to about 70°, and then add a quantity of alcohol equal to one-third the volume of the solution. The authors state that the precipitation of strontium is not quite complete even at the point where a moderately large amount of

calcium begins to precipitate. They did not introduce ammonium salts because the solubility of $SrCrO_4$ was then somewhat increased, and they worked at 70° because the precipitation of $SrCrO_4$ was more rapid than at room temperature.

The method of separation adopted by us is essentially the same as that described by Caron and Raquet, *Bull. soc. chim.* [3], **35**, 1061–1069 (1906). A large number of experiments were performed, however, to determine the best conditions for making the separation. The presence of ammonia and ammonium salts appears to have a greater influence on the solubility of $CaCrO_4$ than on that of $SrCrO_4$, and thus makes the separation more satisfactory than in the method of Fresenius and Ruppert.

Precipitation of $SrCrO_4$ in P. 84. — 1, 0.5, 0.3, and 0.2 mgm. Sr as nitrate were treated in separate experiments by P. 84, 10 ccm. 20% K_2CrO_4 and 10 ccm. 30% acetic acid being first added in each case: in the experiments with 1 and 0.5 mgm. the mixture became turbid at once on adding 50 ccm. alcohol to the ammoniacal solution; in the two remaining experiments the mixtures became distinctly turbid on standing several minutes. Therefore the test is a delicate one, and the precipitation must be nearly complete.

To 500 mgm. Sr as nitrate were added 10 ccm. 30% acetic acid and 10 ccm. 20% K_2CrO_4 solution (*i.e.*, an excess of about 3.7 ccm.), and the mixture was treated by the first paragraph of P. 84: a very large precipitate of $SrCrO_4$ separated. This was filtered off and the filtrate treated by the second paragraph of the procedure, 5 ccm. more K_2CrO_4 solution and 10 ccm. alcohol being added: a precipitate separated at once which was estimated to contain about 20 mgm. of strontium. The filtrate was treated again in the same way: no precipitate separated on long standing, showing that even 500 mgm. of strontium is completely precipitat d in the procedure.

Solution of $SrCrO_4$ on Washing. — 5 mgm. Sr were precipitated as $SrCrO_4$ in P. 84; the precipitate was collected on a filter and washed for a long time with a mixture of equal volumes of water and alcohol. Successive portions of the wash water were tested for strontium by adding K_2CrO_4 and a little NH_4OH: the first 20 ccm. contained considerable K_2CrO_4 and very little strontium; the next 100 ccm. contained about 2.5 mgm. Sr; the next 100 ccm. contained about 1.5 mgm. Sr, and the residue on the filter was estimated to be only about 0.3 mgm. Sr. — The experiment was repeated with 1 mgm. Sr: the first 100 ccm. of wash water contained about 0.5 mgm. Sr and the second 100 ccm. about 0.4 mgm. Sr; the residue could scarcely be seen on the filter, gave only a slight flame test in P. 85, and contained less than 0.2 mgm. Sr.

Precipitation of K_2CrO_4 in P. 84. — A mixture of 10 ccm. 20% K_2CrO_4 solution and 10 ccm. 30% acetic acid were treated by P. 84, the alcohol being added slowly: 50 ccm. alcohol produced no precipitate and the solu-

tion was perfectly clear after the addition of 20 ccm. more alcohol and shaking; 5 ccm. more produced a small precipitate, and on the addition of another 5 ccm. portion, making 80 ccm. in all, the precipitate was large. It dissolved readily on washing. — The experiment was repeated, except that the alcohol (50 ccm.) was added quickly: a precipitate appeared as the alcohol was poured into the solution, but disappeared on shaking the mixture. — The experiment was repeated with 20 ccm. K_2CrO_4 solution instead of 10 ccm.: a permanent precipitate of K_2CrO_4 formed with 40 ccm. alcohol, but not with 35 ccm.

Behavior of Calcium and Magnesium towards Potassium Chromate. — 500 mgm. Ca as pure $Ca(NO_3)_2$, 10 ccm. 20% K_2CrO_4 solution, and 10 ccm. 30% acetic acid were treated by P. 84, 50 ccm. alcohol being added: no precipitate separated in half an hour, and only an insignificant one on standing over night. After pouring through a filter, 5 ccm. more K_2CrO_4 solution and 10 ccm. alcohol were added: a precipitate separated slowly, which after standing several hours corresponded to only several milligrams of calcium. — The experiment was repeated, except that after the addition of the extra K_2CrO_4 and alcohol the mixture was allowed to stand several days: the precipitate separated slowly as before, but was large after several days.

400 mgm. Mg as nitrate, 10 ccm. 20% K_2CrO_4 solution, and 10 ccm. 30% acetic acid were treated by P. 84: the solution remained clear on adding 50 ccm. alcohol, but a very small crystalline precipitate separated out on standing several hours, which was very different in appearance from $SrCrO_4$.

P. 85, N. 1–2: *Action of a Mixture of Sodium Oxalate and Carbonate on Calcium and Strontium Solutions.* — In a series of experiments 5 mgm. Ca as nitrate were added to varying amounts of a 10% Na_2CO_3 solution; 30 ccm. 3% $Na_2C_2O_4$ solution were added, and the mixture boiled for 5 minutes. The precipitate was filtered off, washed well, and a 5 ccm. portion of dilute acetic acid was poured three times through the filter; the residue was dissolved in dilute HCl. The amount of calcium in each solution was estimated by adding NH_4OH and $(NH_4)_2C_2O_4$ and boiling. The results are given in the following table:

Amount of 10% Na_2CO_3 used	2.0	4.0	5	6 ccm.
Amount of calcium in HAc	0.05–0.2	<0.1	1	4.5–5.0 mgm.
Amount of calcium in HCl	4.9	5.0	4	0.0–0.5 mgm.

$CaC_2O_4.H_2O$ was found to be practically insoluble in cold dilute acetic acid; therefore these results show the amounts of calcium present as carbonate and oxalate, respectively. The test with $(NH_4)_2C_2O_4$ enabled 0.05 mgm. Ca to be detected.

Similar experiments were tried with 5 mgm. Sr; 30 ccm. 3% $(Na)_2C_2O_4$ were first added and then in separate experiments 1 ccm. and 2 ccm. 10% Na_2CO_3: in such case all the strontium dissolved in the acetic acid, showing that the strontium oxalate was converted into carbonate in this treatment. SrC_2O_4 was found to be nearly insoluble in acetic acid, and the test with $(NH_4)_2C_2O_4$ scarcely enabled 0.5 mgm. Sr to be detected.

Effect of the Presence of Barium Chromate. — To 5 mgm. Ba as nitrate were added in succession 20 mgm. K_2CrO_4 dissolved in a little water, 30 ccm. 3% $Na_2C_2O_4$, and 2 ccm. 10% Na_2CO_3; the mixture was boiled for 5 minutes and filtered, and the precipitate washed: the precipitate was yellow, showing the presence of some $BaCrO_4$. 5 ccm. dilute acetic acid was poured through the filter, K_2CrO_4 was added, and the mixture boiled: a precipitate corresponding to about 3 mgm. Ba resulted. — The experiment was repeated with 50 and with 100 mgm. K_2CrO_4: not more than 0.5 mgm. Ba dissolved in the acetic acid, showing that in these experiments $BaCrO_4$ was not converted into carbonate, as in the preceding experiment with less K_2CrO_4.

P. 85, N. 3: *Delicacy of Test for Strontium.* — 0.5 and 1.0 mgm. Sr as nitrate were treated by P. 85: satisfactory tests were obtained in each case. — The experiments were repeated, except that the strontium was first precipitated as chromate by P. 84: the results were the same. — In an experiment with no strontium a perfect blank test was obtained. The test with ammonium carbonate enables 0.3 mgm. Sr in the acetic acid solution to be easily detected.

Effect of the Presence of Calcium and Magnesium. — 5 mgm. Ca as nitrate were treated by P. 85, the mixture being boiled for 5 minutes: a perfect blank was obtained. — The experiment was repeated with 10 mgm., the mixture being boiled 5 minutes: the result was the same. — The experiment was repeated three times with 30 mgm. and once with 50 mgm. Ca: in two of these experiments good blank tests were obtained, but in the third and in the experiment with 50 mgm. a small turbidity resulted, corresponding to about 0.3–0.4 mgm. Ca. — No test was obtained with $(NH_4)_2CO_3$ when the acetic acid solution contained 0.2 mgm. Ca. The results obtained above, when calcium was tested for in the acetic acid solution with $(NH_4)_2C_2O_4$, show that this solution always contained 0.05–0.2 mgm. Ca.

50 mgm. Mg as nitrate were treated by P. 85: a small gelatinous precipitate of $Mg(OH)_2$, corresponding to 5–10 mgm. Mg, was obtained, which dissolved in the acetic acid; no precipitate formed in the ammonium carbonate solution in several hours, but a small crystalline one separated out over night.

P. 86, N. 1: *Solubility of $CaC_2O_4.H_2O$ in Water.* — See A. F. Holleman, *Z. physik. Chem.*, **12**, 129 (1893); Kohlrausch and Rose, *Z. physik. Chem.*, **12**, 241 (1893); Richards, McCaffrey, and Bisbee, *Z. anorg. Chem.*, **28**, 85

(1901). According to the last-named authors the solubility is 4.7×10^{-5}, 6.5×10^{-5}, and 9.6×10^{-5} mols per liter at 25°, 50°, and 95°, respectively.

Solubility of $MgC_2O_4.2H_2O$. — According to the conductivity measurements of Kohlrausch, *Z. physik. Chem.*, **50**, 356 (1905), the solubility at 18° is 2.6×10^{-3} mols per liter.

Precipitation of Calcium by Ammonium Oxalate. — 0, 0.3, 0.5, 1.0, and 2 mgm. Ca as nitrate were dissolved separately in 10 ccm. 15% acetic acid, and the solutions were treated by P. 84 and 86, 25 ccm. 4% $(NH_4)_2C_2O_4.H_2O$ solution being added in each case to the hot solution in P. 86: in the experiments with 1 and 2 mgm. the mixtures became slightly turbid at once and the suspended precipitates were very easily seen in a minute or two; with 0.5 mgm. the solution was at first almost clear, but the precipitate could be easily seen after 5 minutes; with 0.3 mgm. a very small precipitate settled out in about an hour; with the solution containing no calcium a good blank test was obtained. In the experiment with 0.5 mgm. the mixture was filtered after about 20 minutes, and the precipitate was tested by P. 87: a small precipitate of $CaSO_4$ separated quickly on adding alcohol to the H_2SO_4 solution.

The experiments with 1 and 2 mgm. Ca were repeated, except that the ammonium oxalate was added to the cold solution: no precipitates separated in the cold, but the solutions became turbid on heating to boiling. The mixtures were shaken and allowed to stand several minutes: the precipitates did not run through the filter. In experiments in which a large amount of calcium was precipitated in the cold filtration was slow, and the precipitate ran through the filter.

Separation of Calcium from Magnesium by Ammonium Oxalate. — 400 mgm. Mg as chloride were dissolved in 10 ccm. 30% acetic acid; the solution was neutralized with NH_4OH (0.90) and an excess of 3 ccm. added; the mixture was diluted to 250 ccm.; 10 ccm. 20% K_2CrO_4 solution and 50 ccm. alcohol were added, making the total volume 310 ccm.; the mixture was heated to boiling and 20 ccm. 4% $(NH_4)_2C_2O_4.H_2O$ solution added: a small precipitate corresponding to about 0.5 mgm. Ca formed. This was filtered off, 15 ccm. more oxalate solution were added, and the mixture was boiled: no more precipitate separated. — The experiment was repeated, except that 1 mgm. Ca as nitrate was also added: a larger precipitate separated than in the former case. This was filtered off and treated by P. 87: a precipitate of $CaSO_4$ separated at once on adding alcohol.

The experiment with 400 mgm. Mg was repeated, except that the total volume of the solution was 210 instead of 310 ccm.: a large precipitate separated on cooling. — This experiment was repeated with 300 mgm. Mg, the total volume being 210 ccm.: the hot solution was clear after adding the ammonium oxalate, but a small precipitate separated on cooling; this pre-

cipitate dissolved when the mixture was heated to about 70°, but separated again on cooling, thus showing that the solubility of the magnesium precipitate increases rapidly with the temperature. — The experiment was repeated with 200 mgm. Mg, the volume being 200 ccm.: no precipitate separated even on long standing at room temperature. These experiments show that the volume should not be less than 300 ccm. when much magnesium is present, but that the volume may be much smaller if the amount of magnesium is small.

P. 87, N. 1: *Solubility of* $CaSO_4.2H_2O$. — For the solubility in water at temperatures between 0° and 100° see Hulett and Allen, *J. Am. Chem. Soc.*, 24, 674 (1902). For the solubility in H_2SO_4 solutions see Cameron and Breazeale, *J. Physic. Chem.*, 7, 574 (1903). The solubility in water in mols per liter at 25° is 0.0153, and there is a maximum solubility of 0.0208 mols per liter in an acid containing 75 grams H_2SO_4 per liter. With rising temperature the solubility in H_2SO_4 increases and the maximum solubility is in more concentrated solutions. The laboratory acid of sp. gr. 1.2 contains 328 grams H_2SO_4 per liter, and the solubility of $CaSO_4$ in it is over half the maximum solubility.

Precipitation of Calcium as $CaSO_4.2H_2O$. — 0, 0.2, 0.3, 0.5, and 1.0 mgm. Ca as nitrate were dissolved in separate experiments in 5 ccm. dilute H_2SO_4 (1 volume 1.20 acid and 3 volumes water), 10 ccm. 95% alcohol were added, and each mixture was shaken: in the experiment with 1 mgm. the solution became turbid at once and a large, flocculent precipitate separated in a minute or two; with 0.5 mgm. the turbidity was distinct in 1 minute, and the precipitate appeared flocculent in 2 or 3 minutes; with 0.2 and 0.3 mgm. the solutions became slightly turbid in 5 minutes, the test was distinct in 10 minutes, and the precipitate appeared flocculent in half an hour; in the blank experiment the solution remained clear. — The experiments were repeated with H_2SO_4 (1.20): the results were the same, except that the calcium precipitated somewhat less rapidly. — Some experiments were performed with more concentrated H_2SO_4, but the results became less and less satisfactory with increasing concentration of H_2SO_4.

P. 87, N. 2: *Behavior of Strontium or Magnesium in the Confirmatory Test for Calcium.* — 10 mgm. Sr as nitrate were precipitated as oxalate by adding NH_4OH, $(NH_4)_2C_2O_4$ and heating; the mixture was filtered and the precipitate washed twice with water. A 5 ccm. portion of H_2SO_4 (1.20) was poured repeatedly through the filter, and finally 15 ccm. 95% alcohol were added to the solution: the mixtures became turbid at once; after settling the precipitates corresponded in amount to that obtained with 0.2–0.3 mgm. Ca. — The experiment was repeated with 2 mgm. Sr as nitrate, which was added directly to 5 ccm. H_2SO_4, various concentrations of H_2SO_4 being used, from 1 volume H_2SO_4 (1.20) in 10 ccm. to H_2SO_4 (1.20): in each case the result was nearly the same as before.

50 mgm. Mg as $MgCl_2$ were dissolved in 5 ccm. H_2SO_4 (1.05) and 15 ccm. alcohol were added: no precipitate separated, even on long standing.

P. 88, N. 1: *The Precipitation of Magnesium by Phosphate.* — In each of a series of experiments 0.5 mgm. Mg as $Mg(NO_3)_2$ was dissolved in 10 ccm. 30% acetic acid, 10 ccm. 20% K_2CrO_4 solution were added, the solution was neutralized with NH_4OH and diluted to 250 ccm.; 50 ccm. alcohol and varying amounts of NH_4OH (0.90) and of 7% $Na_2HPO_4.12H_2O$ solution were added and the mixture shaken. The following table shows the time in which the solution became turbid.

Excess NH_4OH (0.90).	No. Cubic Centimeters 7% $Na_2HPO_4.12H_2O$ Added.		
	10	20	30
3 ccm.	15 minutes	15 minutes	15 minutes
13 ccm.	7 minutes	3 minutes	3 minutes
30 ccm.	. .	2 minutes	2 minutes

In each case the turbidity became more distinct in a few minutes, and a crystalline precipitate settled out in 1–1½ hours. These experiments show that the presence of a considerable excess of NH_4OH makes the precipitation more rapid.

The experiment with 13 ccm. excess NH_4OH (0.90) and 2.0 ccm. 7% $Na_2HPO_4.12H_2O$ was repeated with 0.3, 0.2, 0.1, and 0.0 mgm. Mg, respectively: in the experiment with 0.3 mgm. the solution became turbid in 10 minutes, the test was very distinct in 15 minutes, and a crystalline precipitate collected within 1½ hours; with 0.2 mgm. a slight turbidity appeared in 15 minutes, the test was fairly distinct in 30 minutes, and a small precipitate had collected within 1½ hours; with 0.1 mgm. no turbidity could be seen, but a minute precipitate separated in 2 hours; in the blank experiment there was no turbidity, and no precipitate separated in several hours.

Precipitation of Calcium as Phosphate. — The last experiment was repeated with 2 and with 5 mgm. Ca as nitrate: in the experiment with 5 mgm. the solution became turbid almost at once, and with 2 mgm., slightly turbid, after standing about 1 hour.

***P. 91a, N. 2**: *Precipitation of Lithium as Phosphate.* — To determine the delicacy of the test, 0.3 and 0.5 mgm. Li as LiCl were dissolved separately in 3 ccm. water; 0.5 ccm. 10% NaOH solution and 1 ccm. 10% $Na_2HPO_4.12H_2O$ solution were added; the mixture was heated to boiling in a large test tube, 1 ccm. alcohol was added, and the mixture boiled: a

white precipitate formed almost at once. — The experiment was repeated with 0.2 mgm. Li: even after boiling off a large part of the alcohol the solution was almost clear, but on adding a second portion of alcohol and again boiling a very distinct precipitate was obtained. — A blank experiment was made without adding any lithium: a clear solution was obtained even after adding alcohol and boiling it off four times. — The precipitates obtained in these experiments were filtered off, washed thoroughly with cold NH_4OH (0.96), and dissolved in dilute HCl; the solutions were evaporated to about 1 ccm., and the color imparted to the flame was tried: the red color was easily seen in the experiment with 0.5 mgm. Li, but was not very distinct in that with 0.3 mgm. Li, owing to the yellow sodium flame. By means of a spectroscope, however, lithium was easily detected in both cases.

To determine the effect of the presence of alcohol, the experiment was repeated with 1 and with 2 mgm. Li, except that no alcohol was added; the test tube was heated to boiling and then placed in a steam bath near 100°: with 2 mgm. a precipitate appeared on heating, but with 1 mgm. none appeared in 10 minutes.

Experiments with varying amounts of NaOH and Na_2HPO_4 indicated that the test was most delicate when an excess of 0.3–0.5 ccm. of the 10% NaOH solution and from 1–2 ccm. 10% $Na_2HPO_4.12H_2O$ solution were used.

P. 92, N. 1–2: *Test for Potassium with Sodium Cobaltinitrite.* — For the composition of the precipitate $K_2NaCo(NO_2)_6H_2O$ see Adie and Wood, *J. Chem. Soc.*, **77**, 1076 (1900); Drushel, *Am. J. Sci.* [4], **24**, 433 (1907); **26**, 329 (1908).

0.3 and 0.5 mgm. K as KCl were dissolved separately in 5 ccm. water and 5 ccm. of $Na_3Co(NO_2)_6$ reagent (2 days old) added: the solution became turbid within 1–4 minutes, and precipitates settled out quickly. These were filtered off and washed with water: the yellow precipitate were easily seen on the white filter. — The experiment was repeated with 0.2 mgm. K: in 20–30 minutes the solution was slightly turbid, and the precipitate began to settle out in about 2 hours. The experiment was repeated with 0.1 mgm. K: after 2 hours the solution was clear, but a small precipitate settled out in 6–10 hours. — A blank experiment was made without adding any potassium: the solution remained clear for 2 days.

To determine the effect of the age of the reagent, the experiments with 0.3 and 0.5 mgm. K were repeated, except that an old reagent was used, which had been kept in a stoppered bottle for 4 months: the results were the same.

To determine the effect of the presence of acetic acid, separate 0.5 mgm. portions of K as KCl were dissolved in 5 ccm. of solution containing, respectively, 0, 0.5, 1.0, and 2.5 ccm. 30% acetic acid, and 5 ccm. of the reagent added: in each case the solution became distinctly turbid within 1 minute. —

The experiments were repeated with 0.3 mgm. K: each solution became turbid in less than 5 minutes. Therefore the presence of acetic acid does not decrease the delicacy of the test.

Behavior of $Na_3Co(NO_2)_6$ towards Various Substances. — 2 mgm. NH_4 as NH_4NO_3 were dissolved in 5 ccm. water and 5 ccm. reagent added: the solution became turbid almost at once. — The experiment was repeated with 0.5 and 1 mgm. NH_4: with 1 mgm. the solution became turbid in about 10 minutes; with 0.5 mgm. in several hours. The turbid solutions were almost identical with those obtained when potassium was present, but the precipitate, when filtered off and washed, was found to be more orange in color than the potassium precipitate.

50 mgm. Li as LiCl were dissolved in 5 ccm. water and 5 ccm. reagent added: in 2 days only a minute precipitate settled out, corresponding to about 0.2 mgm. K. — The experiment was repeated with 100 mgm. Li: only a very small precipitate settled out on standing, which was not greater than that expected from the potassium impurity.

50 mgm. of Ca, Sr, Ba, and Mg as nitrate were dissolved in separate experiments in 5 ccm. water and 5 ccm. reagent added: no precipitate formed in 2 hours in any case.

To 5 ccm. of solution containing 1 ccm. 10% NaOH were added 5 ccm. of the reagent: the solution slowly darkened and very finely divided, was almost black in 2 minutes, and when filtered yielded a black precipitate and filtrate.

To 2 ccm. 10% $Na_2HPO_4.12H_2O$ solution were added 3 ccm. water and 5 ccm. $Na_3Co(NO_2)_6$ reagent: no precipitate formed.

To 1 ccm. alcohol and 4 ccm. water were added 5 ccm. reagent: no precipitate formed in 18 hours.

2 ccm. 10% $Na_2HPO_4.12H_2O$ solution, 1 ccm. alcohol, and 2 ccm. water were mixed and treated with 5 ccm. $Na_3Co(NO_2)_6$ reagent and the mixture allowed to stand over night: a film covered the glass and some crystals adhered to it. On filtering and washing, the film was found to be light violet and the crystals somewhat darker; on dissolving in HCl both were found to contain cobalt. — The experiment was repeated, except that the mixture was evaporated almost to dryness, to expel the alcohol, and then dissolved in 5 ccm. water before adding the $Na_3Co(NO_2)_6$ reagent: there was practically no precipitate, even on long standing.

P. 93, N. 1: *Effect of the Presence of Potassium Salts on the Test for Sodium.* — Neutral solutions of various mixtures of potassium and sodium, both as chlorides and nitrates, were evaporated in small flasks to about 1 ccm., and cooled. In each case 2 ccm. of the $K_2H_2Sb_2O_7$ reagent (P. 94, N. 1) were added; the mixture was shaken to dissolve any KCl or KNO_3 that had separated on cooling, and allowed to stand for several hours. The

following table shows the number of milligrams of sodium present in each experiment.

	Chlorides.			Nitrates.		
Test for Na.	In 10 minutes.	Over night.	Failed.	In 10 minutes.	Over night.	Failed.
300 mgm. K . . .	10	7	6	. .	6	4
200 mgm. K . . .	5	4	3	. .	3	. .
100 mgm. K . . .	3	2	1	. .	2	1
50 mgm. K . . .	2	2	1	. .	. .	. .
0 mgm. K . . .	1	. .	. .	1	. .	. .

It is evident that the presence of KCl and of KNO_3 greatly decreases the delicacy of the test for sodium.

The experiments with 300 mgm. K were repeated, except that a large part of the K was separated as K_2SO_4 by the process described in P. 93: with 3 mgm. Na a very satisfactory test was obtained in 15 minutes; with 2 mgm. Na a few small crystals separated on standing over night, but the test was practically a failure. In another experiment with 200 mgm. K and 2 mgm. Na a distinct test for sodium was obtained in about 2 hours.

P. 93, N. 2: *Action of Potassium Pyroantimonate on Lithium.* — In separate experiments 2, 5, and 10 mgm. Li as LiCl were treated by P. 94: in each experiment a crystalline precipitate very similar in appearance to $Na_2H_2Sb_2O_7.6H_2O$ separated — with 10 mgm. in a few minutes, with 5 mgm. in about 1 hour, and with 2 mgm. in 10 hours. The experiment was repeated with 1 mgm. Li: no precipitate separated in 24 hours, and only a very small one in 3 days. — The experiments were repeated with freshly prepared $K_2H_2Sb_2O_7$ reagent, to which no KOH had been added: the results were the same.

P. 93, N. 2–3: *Precipitation of Lithium and Sodium as Fluorides.* — 1 mgm. Li as LiCl was dissolved in 2 ccm. water, 1 ccm. NH_4OH (0.90) and 2 ccm. 20% NH_4F solution were added; a small precipitate separated in a minute or two, and was proved to be lithium by the flame test and by converting it into Li_3PO_4 by *P. 91*a*. — The experiment was repeated with 1 and with 2 mgm. Li except that the initial volume was 5 ccm. instead of 2 ccm.: a very distinct precipitate of LiF separated at once with 2 mgm., but the precipitate with 1 mgm. after an hour was so small that the test with Na_2HPO_4 failed.

The above experiments were repeated with 100 mgm. Na as NaCl: in the smaller volume a precipitate of NaF formed at once; in the larger volume no precipitate separated.

Experiments with 0.5 mgm. Li showed that this amount could be detected by evaporating the solution to 0.5 ccm., adding 0.5 ccm. NH_4OH (0.90) and 1 ccm. 20% NH_4F solution, but that 0.5 ccm. was then about the limit of detectability. Under these conditions a precipitate of NaF was obtained at once with 30 mgm. Na as NaCl, but not with 20 mgm.

For the precipitation of lithium as fluoride and the detection of sodium in the filtrate see **T. A. 219–221.**

P. 93, N. 4: *Separation of Sodium and Lithium by Alcohol Ether.* — Mixtures of chlorides of sodium and lithium were treated by the process described in the note. The lithium was confirmed by *P. 91*a*; the sodium by P. 94, including the flame test. The results are recorded as in the Test Analyses.

No.	1	2	3	4	5	6
Na	200 S	200 —	200 —	0 S	2 S	1 S—
Li	0 S	1 S	0.5 S—	100 —	100 —	100 —

In making the flame test for sodium in No. 6, the yellow flame had a reddish tinge and the spectroscope showed the presence of lithium; on standing about 24 hours a few small crystals separated in the test for sodium in No. 4, but the flame was red, not yellow. In these analyses the lithium had not been carefully washed out of the filter paper.

P. 94, N. 1–2: *Composition of Alkali Antimonates.* — Several different solid antimonates of each element are known, and formulæ have been assigned chiefly from their behavior when heated. Thus the ordinary compounds of sodium, which has the composition $NaSbO_3.3\frac{1}{2}H_2O$, loses water when heated, but the last half molecule remains even at 350° — Knorre and Olschewsky, *Ber.*, **18**, 2360 (1885). The three molecules that are given off readily are considered to be water of crystallization, and the remainder to be chemically combined; the formula is therefore written $Na_2H_2Sb_2O_7.6H_2O$. The question of the composition of the solutions is still an open one.

Test for Sodium with Potassium Antimonate. — 1 mgm. Na as NaCl was dissolved in 1 ccm. water and 2 ccm. of the freshly prepared alkaline potassium antimonate reagent (see N. 1) were added: after 5 minutes a small, nearly colorless precipitate adhering to the glass could be seen, which in 15 minutes had become much more distinct and in 30 minutes had become white and opaque. As it adhered very firmly to the glass the solution was

poured out; the precipitate was washed with water several times, and finally the test tube was filled with water: after several hours the precipitate still remained on the glass. The water was poured out and HCl added: the precipitate dissolved, more rapidly on warming. — The experiment was repeated several times with 0.5 mgm. Na: in 30–60 minutes small, colorless crystals were seen adhering to the glass, which became more distinct on standing 30–60 minutes longer, though the precipitate remained nearly colorless.

To determine the effect of the amount of antimonate used, the foregoing experiments were repeated, using different reagents, in which 1, 2, 3, 5, and 8 grams pyroantimonate were added to 100 ccm. boiling water, after which the solutions boiled for a minute or two until almost all the salt disappeared. The results are given in the following table. In each case the sodium chloride was dissolved in 1 ccm. and 2 ccm. of a reagent were added.

Pyroantimonate in 100 ccm.		1 gram.	2 grams.	3 grams.	5 grams.	8 grams.
2.0 mgm. Na	slight test in . .	5	2– 5	3	10	10 minutes
	distinct test in .	5–30	5–30	5	15	30 minutes
1.0 mgm. Na	slight test in . .	7–10	5	5	20	10–60 min.
	distinct test in .	30–60	10–30	10–30	60	Over night
0.5 mgm. Na	slight test in . .	. .	30–60	30–60	No test in 1 hour	. .
	distinct test in .	90 minutes	60–90	60–90		. .

It is evident that the second and third reagents give the most satisfactory results. The former is the one recommended in the process.

Effect of the Alkalinity of the Potassium Pyroantimonate Reagent. — A solution was prepared from 2 grams of the commercial salt and 100 ccm. water as described in N. 1, but no KOH was added: it was clear and reacted neutral to litmus paper. To a portion a few drops of HCl were added: a white, flocculent precipitate separated quickly. — The neutral (2%) solution was placed in a corked test tube and allowed to stand: it remained clear over night, but after a few days a white, flocculent precipitate separated out. The clear solution was poured off and again allowed to stand: a precipitate again formed, which ran through the filter. After 6 weeks 2 ccm. of the solution were added to 1 ccm. of a NaCl solution containing 2 mgm. Na: no crystalline precipitate formed, even on standing several hours. The solution now reacted alkaline to litmus paper.— Various other strengths of the

reagent were tested in the same way, portions of the solutions being set aside before KOH was added: the 1% solution was neutral and decomposed very slowly; the 3% solution showed a very slight alkaline reaction and decomposed more rapidly than the 2% solution; the 5 and 8% solutions were distinctly alkaline, became very turbid over night, and large precipitates separated on standing.

To try the effect of the presence of KOH, a solution of the antimonate reagent was prepared by dissolving 2–3 grams of the salt in 100 ccm. boiling water and cooling; and to three 20 ccm. portions of the neutral solution were added, respectively, 0.5, 1.0, and 2.0 ccm. 10% KOH solution. These solutions were placed in corked test tubes and set aside: a flocculent precipitate separated slowly in each solution, but it was much smaller than that obtained in a corresponding solution to which no KOH had been added. After 6 weeks 2 ccm. of each solution were added to 1 ccm. portions NaCl solution containing 1 or 2 mgm. Na: a small but distinct crystalline precipitate separated in each case,— within 10 minutes with 1 mgm. Na, and within 3–5 minutes with 2 mgm.; the tests became more distinct on standing. The clear reagents were allowed to stand 3 months longer: a very small, flocculent precipitate separated in each case. The tests with 1 and 2 mgm. Na were then repeated: the results were exactly the same. A comparison of these results with those obtained above with freshly prepared solutions shows that an alkaline reagent, unlike a neutral reagent, does not deteriorate appreciably in over 4 months.

The tests with 1 and 2 mgm. Na were repeated with a freshly prepared reagent to which no KOH had been added: the results were almost exactly the same, showing that the delicacy of the test is not affected by the presence of alkali, nor by its amount.

About 3 grams of antimonate were added to 100 ccm. 0.3 to 0.5% solution of KOH, the mixture was heated to boiling, shaken well while hot, cooled, and filtered. 2 ccm. of this reagent were added to 1 ccm. NaCl solution containing 3 mgm. Na: no precipitate separated in a day, showing that the KOH must not be added to the solution until after it is cooled.

Behavior of Potassium Antimonate Reagent towards Various Substances.— In the following experiments the substance was dissolved in 1 ccm. water and 1 to 2 ccm. of the antimonate reagent added.

With 5 mgm. NH_4 as NH_4NO_3, in slightly alkaline solution, a small, flocculent precipitate separated on standing an hour or two, but did not increase on longer standing.

With 1 mgm. Ca as nitrate a large, white, gelatinous precipitate formed at once; with 0.2 mgm. Ca, marked turbidity at once; with 0.1 mgm. Ca, slight turbidity at once.

With 0.2 mgm. Ba as nitrate a slight turbidity appeared at once; with

0.1 mgm. Mg as nitrate, a slight turbidity at once; with 0.3 mgm. Mg there was a marked turbidity.

In a number of experiments 400 mgm. Mg as nitrate were precipitated as magnesium ammonium carbonate by P. 81, and the neutral filtrate tested for Na by P. 93: in one or two cases a perfect blank was obtained, but in others a small, flocculent precipitate separated corresponding to 0.1–0.3 mgm. Mg. But this turbidity was probably not due to magnesium, since in another experiment no precipitate separated when KOH was added to the filtrate; and yet a small, flocculent precipitate was obtained on adding the antimonate.

A few drops of alcohol were added to 1 ccm. of reagent: a large, white precipitate separated at once.

THE RÔLE OF VISCOSITY IN AIR SUPPORT OF A MOVING AËROPLANE

By FRANK W. VERY

LANGLEY, in his "Experiments in Aërodynamics," says (page 105), in summing up the results of his work, "that the pressure [on a moving aëroplane] is normal to the inclined surface, and hence that the effects of skin-friction, viscosity, and the like are negligible in such experiments." This involves a mistake. Viscosity, instead of being negligible, is the principal factor in the supporting power of aëroplanes at low angles. In making this criticism I wish to add that, so far as I know, this is the only serious mistake in the whole book, and it is one of interpretation, but not an error in the data of experiment. It should be noted that the statement that the pressure is normal to the inclined surface is an inference, since the observations did not have the minute precision necessary to establish this point beyond a doubt. Other considerations permit us to overturn this inference and to state that the direction of pressure differs slightly from the normal at low inclinations.

In the lateral movement of an inclined plane the stream lines enclose a partial vacuum behind the advancing edge, but the lifting power of the vacuum is small compared with the sustaining effect due to the inertia of the air. Thus in some experiments which I tried while working with Professor Langley I found that when a plane has its front edge inclined downward in the direction of advance by 7°, in which case the vacuum due to the stream lines is on the lower side of the plane, the time of fall when the plane was moving forward at velocities near 10 meters per second was still slightly greater than when the fall was from a position of rest, indicating that the downward pull of the vacuum produced by motion was not equal to the support obtained through viscosity. If the vacuum effect is incapable of overcoming viscosity in a solid plane, still less can there be any great amount of suction in the case of a bird's wing, which is an open-work structure permeable to air. Consequently the explanation of the soaring bird

as an instance of support of weight by a vacuum, which has been proposed by some theorists, will not work.

To Langley more than to any one is due the credit for demonstrating the part which the inertia of the air plays in supporting a bird. Not that he was the first to put forth this explanation, although one might suppose this to be the case from some passages in his paper on "The Internal Work of the Wind," nor is he always correct in all of the details. Thus in this paper he attributes a selecting power to the bird, which, by rotating the plane of its wings about a vertical axis, can accumulate energy from variations of the wind. He says: "The rotation of the body about a vertical axis, so as to change the aspect of the inclination, may be illustrated by the well-known habit of many soaring birds of moving in small closed curves or spirals; but it may also be observed, in view of the fact that even in intervals of relative calm, during which the body descends, there is always some wind, that in making the descents if the body, animate or inanimate, maintain its direct advance, this wind tends to strike on the upper side of the plane or pinion. Mr. G. E. Curtis offers the suggestion that the soaring bird avoids such a position when possible, and therefore turns at right angles to or with the wind, and that this may be an additional reason for his well-known habit of moving in spirals." The case is quite different here from that of vertical circling. The latter, or circling in a vertical plane, as explained by Basté, does appear to have an element of choice on the part of the bird. Not so the horizontal circling; for, as the bird rotates at a uniform rate of turning while the fluctuations of the wind are not uniform, the two variations will seldom coincide. The horizontal circling is solely to produce alternations in the relative velocity, which can be done even if the wind remains steady.

If a bird wishes to hover over a given spot on the earth's surface, it must receive the wind on the back in the alternate positions and move alternately faster and slower than the wind. It cannot ascend progressively under these circumstances, but can only balance up and down through a small range. If, however, the bird moves on in the same direction as the wind, its velocity need never fall below that of the wind. The fact that a bird can mount indefinitely by circling in a wind which exceeds a certain speed, determined by the form of the bird, proves that energy can be stored up in this way. This reserve power can only be derived from the wind. Momentum is transferred

from the moving air to the heavier body through the intermediation of the viscosity of the air, augmented in this case by the intimate hold which the multitudinous capillary surfaces of the plumage affords. If the bird chooses to expend only a part of its reserve, the animal may always preserve an actual velocity greater than that of the wind, though this does not mean that it will progress as fast in respect to a rectilinear course.

Babinet thought that he had demonstrated that a bird weighing 1 kilogram, for example, must perform continuously a work of 4.9 kilogram-meters per second in order to support itself in the air. He reasoned thus: "Gravity, acting on the bird, will make it fall 4.9 meters in the first second. It is necessary then that the bird, in order to fly horizontally, shall expend each second the work needed to raise its own weight through 4.9 meters." André, Mayor, and d'Esterno showed the fallacy of this. They say: "If instead of one second Babinet had taken two seconds for his unit of time, he would have found that the bird, falling in this time $4.9 \times 2^2 = 19.6$ meters, must raise its own weight 19.6 meters in two seconds, or 9.8 meters in one second. This work is twice as great as that which the calculation based on the second as the unit of time would give. Thus d'Esterno concluded it was necessary to assign the true value to the time during which the bird is submitted to the accelerating force of gravity. Choosing for a type a bird which gives five wing-beats per second, he estimates that each of the falls, being only able to last a fifth of a second, will be reduced to 0.2 meter. The work which will compensate the effect of these falls during an entire second will consist only in raising the bird five times each second through 0.2 meter, or to a height of 1 meter." These opinions are quoted by Marey in his work on "The Flight of Birds." Marey himself, however, concludes that even this evaluation of the work is exaggerated. He says: "Reason, as well as experience, shows that the bird does not fall during the lowering of the wing. We can therefore assign to the fall of the bird only about the half of a revolution of the wing, or one-tenth of a second. . . . With this correction the fall of the bird is reduced to 0.049 meter five times per second, or 0.245 meter in one second."

But actually even Marey's estimate is exaggerated. Langley says that viscosity is negligible, and his statement has been widely quoted and seems to be generally accepted. But viscosity cannot be neglected, for it is only through viscosity that a moving plane takes hold of a

vein of air of more than its own width; and therefore a consideration of viscosity is necessary as a basis for Langley's own theory of the supporting power of the inertia of the air.

I find for the air pressure on 1 square meter of normal surface, moving with a velocity of 1 meter per second,

at 16° C., $k\Delta P = 0.082$ kilogram per square meter,

at 0° C., $k\Delta P = 0.076$ kilogram per square meter,

each from twenty-two observations. The figures are a little smaller than they would be for sea level, because the barometer was below normal. Now hot air is lighter than cold air and, other things being equal, should give less pressure. It will be seen that, on the contrary, $k\Delta P$ is larger for hot air. The reason is because viscosity is greater at higher temperature, and thus the plane grasps more air.

The unit of time which ought to be taken in Babinet's computation is the time required to transfer the weight of the bird from one mass of air, to which motion is being imparted, to a new mass not yet affected. The distance between these masses depends on wing dimensions. It is relatively less for a narrow wing. The time of transfer depends also on the velocity, and the time-unit in question, or what may be called the natural time-unit for flight, is shorter the greater the velocity and the narrower the wing. Thus at very high speeds the need of exertion for lifting the weight becomes vanishingly small, and at the soaring speed it changes sign.

Langley computed the skin friction of the air on a moving plane by a formula given by Maxwell, and concluded that it must be very small. He says: "There is now, I believe, substantial agreement in the view that ordinarily there is no slipping of a fluid past the surface of a solid, but that a film of air adheres to the surface, and that the friction experienced is largely the internal friction of the fluid, *i.e.*, the viscosity. Perhaps the best formula embodying the latter is given by Clerk Maxwell in his investigation on the coefficient of the viscosity of the air. This is $[\eta =] \mu = 0.0001878\ (1 + 0.0027\theta)$, μ and θ being taken as defined in his paper on the dynamical theory of gases in *Phil. Trans.*, **157**. By this formula the actual tangential force on a 1-foot square plane, moving parallel to itself through the air at the rate of 100 feet a second, is 1,095 dynes (0.08 poundals), or less than one-fiftieth of 1 per cent. of the pressure on the same plane moving normally at this speed, and hence theory as well as observation shows its negligibility" ("Experiments in Aërodynamics," footnote, page 9).

I shall presently consider the applicability of the formula to the problem; but, waiving this consideration for the time being, we may note that the numerical value of the coefficient of viscosity is probably a little smaller than that given by Maxwell. The best experiments give values of the coefficient (η) for air from 0.000172 to 0.000178 in C. G. S. units at 10° C. Assume $\eta = 0.000175$. Then for a 1-foot square plane (both faces) the area (A) is 1,858 square cm., and a velocity (V) of 100 feet per second is 3,048 cm. per second, giving the energy necessary to overcome the pressure of viscous resistance, if $F = \eta A V \times f(a)$, where $f(a)$ is a function of the relative linear dimension of the plane in the line of sight, or what Langley has called the "aspect" of the plane, which is unity for a square plane,

$$F = 0.000175 \times 1{,}858 \times 3{,}048 = 991 \text{ ergs},$$

which is not essentially different from the value given by Langley.

It will be observed that no factor appears in this formula for the linear depth of the viscous layer (l). In theory the expression is to be divided by l, and in the dimensional formula for viscosity, $\frac{M}{LT}$, this division by L is indicated; but determinations of viscosity derived from the flow of gases through small capillaries in which l is very small, and those from the decrement of oscillating plates separated by much larger distances, are so nearly the same, that the effective depth demanded by the theory is evidently one of microscopical dimensions far within the depths of the experimental layers, and thus l is included in the numerical value of η determined by experiment. The process of molecular transfer of energy must be many times repeated within the experimental layer, and as long as the operation is fairly uniform throughout the layer, so that the velocity in a capillary tube increases regularly from the wall to the longitudinal axis of the tube without the formation of complex vortices and striæ, which only happens at low speeds, there is no need to consider the linear depth of the layer.

The case becomes different in dealing with extensive surfaces of superposed aëroplanes moving at high velocities, generating embracing stream-line envelopes of air in complex, vortical motion. Here the effective radius of the disturbed condition of the air is of importance. A narrow plane, say 2 inches wide, presenting the aspect of its longer dimension, creates by its motion through the air a region of vortical disturbance perhaps 2 feet wide — in fact, presumably much wider if

we consider the totality of minute motions constituting the wake; but the distances given are sufficient for practical considerations.

I may refer to an experiment by T. E. Stanton [1] in which a 2-inch square disk in an air current through a tube 2 feet in diameter just began to experience reaction from the walls of the tube. Langley found that superposed, horizontal, or only slightly inclined planes did not interfere so long as they were separated by vertical distances equal to their dimension in the line of flight. This, however, does not give the depth of the total disturbed layer, for the air shell controlled by the combined system extends to much greater distances.

The formula for viscosity is not as simple as the equation just given would indicate. It might have been surmised that if the viscosity of air is due to collisions of molecules, it would be influenced by the density of the air, since the mean length of the free path depends on the density. On the contrary, there is no influence whatever. This can only mean that the molecules are so nearly completely elastic that, the number of transfers in the layer being finite, it makes no difference how many times they collide in the given space. The transfer of momentum from one part of the gas to another is perfect, in so far as it depends on simple motions of individual molecules, and is only disturbed by the motion of air currents which may be highly irregular.

The salient fact in regard to gaseous viscosity is that it varies with the absolute temperature, that is, with the molecular velocity; not, however, with the first power of the temperature, as Maxwell supposed. Professor Holman obtained for air the formula,

$$\frac{\eta_t}{\eta_o} = 1 + 0.002751t - 0.00000034t^2$$

between the temperature limits 0° and 100° C., t being the centigrade temperature. This result shows that viscosity increases with the temperature, but at a diminishing rate, the reason for the diminishing rate being, as Sutherland shows,[2] that the spheres within which collisions must occur, owing to the perturbations of molecular attraction, are smaller at the higher molecular velocities. The same cause affects the mean free path of the molecules independently of its variation from change of density.

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[1] Institute of Civil Engineers, Proceedings, 136, 3 (1903).

[2] W. Sutherland, "The Viscosity of Gases and Molecular Force," Phil. Mag., Series 5, 36, 507 (1893).

In the formula which has been given above for air friction, V, the velocity, appears in the first power. If we confine our attention to internal friction of the air and let $v =$ *molecular* velocity, Sutherland demonstrates that, while the viscosity effect would vary as the first power of v if the molecules had no attraction for each other, the number of molecular impacts is increased by the deflection of molecules through their mutual attraction when at close quarters. On this account the exponent of v must be increased to at least 1.5 for air. In Meyer's formula,

$$\eta_t = \eta_o(1 + \alpha t)^n,$$

where η_t and η_o are the coefficients of viscosity at temperatures t and 0°, α is the coefficient of expansion, t the centigrade temperature, and n a number to be determined by experiment, Holman found $n = 0.77$. Since absolute temperature is proportional to the square of molecular velocity,

$$\eta \propto T^{\frac{1}{2}} \propto v^{2 \times \frac{1}{2}}.$$

This is close enough for a first approximation, since n varies slightly with the temperature.

The velocity on which internal friction depends is that of the gaseous molecules, in comparison with which the moderate speed of an aëroplane may be neglected. In taking an equation, originally derived from the theory of molecular motions and dealing with microdimensions, and transferring it to macrodimensional motions, there is opportunity for discrepancies to arise. The viscous resistance has not hitherto been distinguished from the skin friction, which includes the infinitesimal slip of the air on the solid surface as well as the slip of an enormous number of successive air layers on each other, because they are inextricably entangled. Although the internal friction of the air is practically independent of the velocity of the aëroplane, the slip of the air on a solid surface, or, what amounts to the same thing, on an adherent film of virtually "solid" air, is not unaffected by changes of speed. As the speed increases, the slip of successive air layers on one another is relatively less, and the sustaining power of an aëroplane or the thrust of an air propeller become greater, the higher the speed. It is the variation of surface slip, or rather of the slip of successive air layers parallel to the surface, which we measure in experiments with air propellers moving at varying speeds. Both the portion of air immediately struck by a moving inclined plane, and that on which motion is less directly impressed through internal friction, receive momentum from

the moving solid, transferring the pressure of the heavy solid to an extensive body of air, whose horizontal area increases with the speed, thereby greatly increasing the efficiency of the aëroplane as a supporting body. Eventually, as speed still further increases, slip will presumably cease entirely; but the air will then behave as a rigid body, *more* power will be needed to force the plane through the air, and its supporting efficiency, after reaching a maximum, must diminish at still higher speeds. When slip ceases, the interaction between the aëroplane and the air through which it moves consists in a transfer of a certain amount of momentum per unit of time to a definite mass of air. The mass of air affected is proportional to the velocity, and so is the momentum. Consequently the energy expended is proportional to the square of the velocity; but where there is slip, less momentum is transferred, and the energy involved is proportional to a power of the velocity less than the square.

Dr. A. F. Zahm[1] has experimented with pine boards, 25½ inches wide and 1 inch thick, in a tunnel 6 feet square, the suspended boards being exposed to air currents flowing parallel to their lengths at speeds between 5 and 40 feet per second, obtaining the tangential force from combined skin friction and internal friction of the air when the linear dimension (l) in the line of flow varies between 2 and 16 feet. For a square plane the measures give a tangential stress of 0.00052 pounds per square foot, for $V = 10$ feet per second. If A is the area of the plane (both faces), a the aspect or ratio of the dimension of the plane in the line of motion to its transverse dimension, and V the velocity of the plane, the total friction in C. G. S. units is,

$$F = 0.0000632 A a^{-0.064} V^{1.85}.$$

For a turbulent current the slip appears to vanish and the exponent of V becomes 2. This formula contains no factor for depth of air layer, evidently because the section of the tunnel exceeded the effective dimensions of the active layer.

The progress attained in researches on viscosity has been through a series of imperfect conceptions, including some misconceptions, and their partial rectification. The supposition that *molecular* velocity enters as the first power into the equation was a misconception; but owing to slip, experiments were satisfied for low velocities by taking

[1] "Atmospheric Friction on Even Surfaces," Phil. Mag., Series 6, **8**, 58 (1904).

an equation of the same form and letting V, the surface velocity, enter as the first power. With higher velocities (meters per second instead of millimeters per second), V becomes $V^{1.85}$, and when the motion is highly turbulent, V^2. A more complete molecular theory also indicates that in the formula for internal friction the molecular velocity appears as $v^{1.5}$. To take a formula devised to express the relation between a tangential stress and temperature, in which it might be permissible to substitute *molecular* velocity for temperature, if the formula were correct otherwise, and then to substitute surface velocity in place of molecular velocity, can only give an erroneous result.

Substituting Zahm's formula for Maxwell's in a recomputation of the energy needed to overcome the friction of a 1-foot square plane moving tangentially at a velocity of 100 feet per second, we get

$$F = 0.00000632 \times 1{,}858 \times (3{,}048)^{1.85} = 32{,}760 \text{ ergs},$$

which is thirty-three times as large as the 991 ergs given with the best values by the erroneous formula.

Maxwell's coefficient of viscosity and the values of η given in physical tables, such as those of Landolt-Börnstein (except under a special condition to be noted presently), are not absolute coefficients of the friction of a moving gas against a solid wall, but are relative numbers serving to connect the internal friction of the gaseous molecules with temperature for various substances. They can readily be converted into absolute coefficients of friction by comparison with that for air whenever the latter shall have been determined with sufficient precision.

It is important to note that in experiments on the flow of gases through tubes, the head, or pressure, required to produce a given velocity through an orifice, or through a short pipe whose friction may be neglected, must be distinguished from the difference of pressure needed to overcome the friction against the walls of a long tube. Let $\Delta P =$ difference of pressure per unit area of section at the ends of a tube of length l, $S = \pi r^2 =$ section of tube, $A = 2\pi rl =$ area of walls of tube, $V =$ linear velocity $=$ volume of flow $\div$ section, $F = S\Delta P =$ frictional resistance, $H =$ absolute coefficient of air friction on a solid surface. Then, accepting Zahm's determination of the exponent of V,

$$H = \frac{F}{A V^{1.85}} = \frac{r\Delta P}{2lV^{1.85}}.$$

From the values of air friction commonly accepted by engineers, given by Thomas Box in his "Practical Treatise on Heat" (page 117), I have selected various values and have computed from them the values of the absolute coefficient of air friction obtained by the preceding formula.

Diameter.	Section.	Velocity.	$H \times 10^8$.
Inches.	Square centimeters.	Centimeters per second.	
⅛	0.316	1,491	8.58
⅜	0.713	662	7.59
¾	2.85	166	6.18
1	5.06	93	5.65
1¼	7.92	596	7.53
2½	31.7	149	6.09
4	81.1	582	7.46
8	324.0	146	6.04
12	730.0	647	7.59
24	2,918.0	162	6.17
36	6,566.0	719	7.69
60	18,241.0	259	6.60

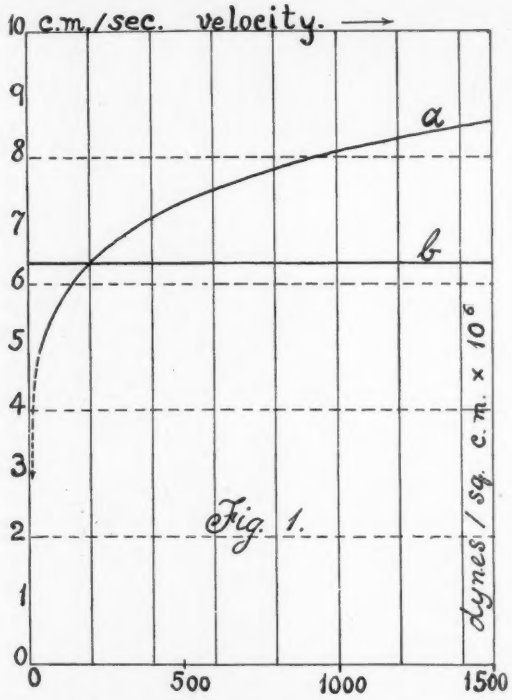
The value of H varies with the velocity from 5.6×10^{-6} for a velocity of 1 meter per second to 8.6×10^{-6} at 15 meters per second (Fig. 1, Curve *a*). Taking a mean of all of the values of H in the preceding table and comparing it with the value obtained by Zahm,

$H = 0.00000693$ from flow of air through tubes (Box),

$H = 0.00000632$ from flow of air over planes (Zahm).

The agreement between these values, in spite of the differences in the forms of the surfaces and in the methods by which they were obtained, guarantees the reliability of the result. The measures also lead us to expect a progressive divergence between the values of H given by the two methods at still higher velocities. Zahm's value, having been obtained with plane surfaces, is to be preferred for aëroplane problems. For such surfaces Zahm found that the coefficient of air friction is a

constant (Fig. 1, Curve *b*). It seems probable that this apparent constancy is due to the summation of two different effects, namely, the edge resistance and the skin friction, which interact in a reciprocal manner, their sum being a constant, while pure skin friction is to be represented by a curve. There is evidently a discontinuity in the *HV*



RELATION BETWEEN THE ABSOLUTE COEFFICIENT OF AIR FRICTION ON A SOLID SURFACE (H) AND THE LINEAR VELOCITY

a from measurements of flow through tubes. *b* from flow of air over planes.
Abscissæ = velocity in cm./sec. Ordinates = stress in dynes/sq. cm. ($\times 10^6$)

law at low velocities, and experiments are especially needed in this intermediate region. Osborne Reynolds has determined the limit of velocity at which turbulence begins for liquids moving through tubes of small diameter, and Couette (*Annales de Chimie et de Physique* [6], 21, 433) has done the same for moving surfaces of concentric cylinders, finding that, with surfaces separated by 2.5 mm., the frictional resist-

ance for velocities greater than about 90 cm. per second becomes proportional to the square of the velocity; but below this speed the frictional resistance varies as the first power of the velocity. Similar measures are needed for air to give the velocity at which the law changes.

Although the relation between viscosity and temperature represented by what may be called Maxwell's equation for η, $\eta = a(1 + bt)$, where a and b are numerical constants and t is the temperature, is independent of the air pressure, it does not follow that the momentum transferred from an aëroplane to the air[1] by virtue of the air's inertia and by means of viscosity is similarly independent of the pressure. It is hardly necessary to point out that the inertia of a given volume of air is proportional to its density, and that pigeons thrown out of a balloon at a great height are unable to fly in the rare atmosphere, but fall helpless. The value of H just given is for air of normal density. Other things being equal, the frictional resistance of the air to the motion of an aëroplane is proportional to the mass of air set in motion, which again depends upon the density of the air.

The distinction to be observed between the transfer of momentum from a solid to a fluid, and its transfer from one body of air to another, is that in the former case the momentum of the solid is that of a body in which mass and volume are proportional, and neither mass nor volume is dependent on air pressure; while for the air masses the volumes and pressures are in inverse relationship and the mass of a given volume varies with the pressure. The transfer of momentum from a moving solid to the air by means of viscosity is the imparting within a specified time of the momentum pertaining to a definite volume of solid substance to a much larger volume of air whose mass is *not* independent of the pressure. Here the amount of momentum transferred, other things being equal, is proportional to the density of the air; but the transfer of momentum from one portion of air to another is more easily accomplished if the air be rare (provided it is not so rare as to have entered on the ultragaseous stage of exceptionally large, free path), while the amount of momentum transferred is proportionally less, so that the result is independent of the density.

Dimensionally, viscosity is $\frac{M}{LT}$, and is a stress given in C. G. S.

[1] The momentum imparted to a particular body of air is handed on to other portions of the medium. It may be dissipated thermodynamically by diffusion and conduction, or the pressure may eventually be transferred to the surface of the ground or to the walls of a containing chamber. In any case the given momentum exists as such only temporarily in the fluid.

units in dynes per square centimeter. Multiplying by the area, we have $\left(\frac{M}{LT}\right) \times L^2 = \frac{ML}{T}$ to represent the momentum transferred through a surface from a moving solid to air, or *vice versa;* and this, multiplied by a velocity, gives $\frac{ML^2}{T^2}$ as the dimension of the work involved in overcoming the viscous resistance ($F = HAV$). If this were the whole process, the product, viscosity × area × velocity, would give the energy expended in producing the motion of an aëroplane; but a further and, in general, a very much larger amount of work has to be performed in generating turbulent motion of the air.[1]

Exception must be made to the law of gaseous friction founded on experiments on the flow of air at considerable speed, and to the absolute coefficient of air friction (H) appropriate to this motion whenever the speed is so slow that there is time for a complete redistribution of molecular velocities, and for the establishment of a stable and uniform gradient of speed within the depth of a layer of gas only a few times the length of the mean free path of the molecules. Under these conditions the viscous resistance is proportional to the velocity of the moving surface, and Maxwell's coefficient (η) applies.

A small drop of water falling through the air, under the attraction of gravity, increases its velocity until a maximum speed is reached, determined not by the mass of the drop, but by the area of its surface and the viscosity. This maximum velocity of fall, or, what is the same thing, the velocity of an upward air current which will just overcome the downward pull of gravity and maintain the drop suspended at a constant height, is given by a formula due to Sir George G. Stokes,[2]

$$v_{max.} = \frac{2}{9} \frac{gr^2}{\eta},$$

[1] As was recognized by Stokes in the footnote to p. 99, Vol. I. of his collected papers.

[2] The original equation is contained in the great memoir by Stokes, "On the Effect of the Internal Friction of Fluids on the Motion of Pendulums," in the Transactions of the Cambridge Philosophical Society for 1850, and may be found in his Mathematical and Physical Papers, 3, 60, equation 127,

$$V = \frac{2g}{9\mu'} \left(\frac{\sigma}{\rho} - 1\right) a^2,$$

where g is the force of gravity, a the radius of the sphere, σ and ρ the densities of water and air, respectively, and where μ' is what Stokes calls the "index of friction," being what we now call the "coefficient of viscosity," divided by the density of the fluid. Since the date of this memoir it has been proved that the viscosity of compressible fluids is independent of the pressure. Consequently it is now appropriate to give the formula in an emended form. The factor $(\sigma - \rho)$ differs so little from unity that it may be omitted, as I have done in the text.

in which g is the acceleration due to gravity, r the radius of the drop, and η is Maxwell's coefficient of viscosity. If $\eta = 0.000175$,

$$v_{max.} = 1.246 \times 10^6 \times r^2.$$

This agrees well enough with observation for spheres up to about $\frac{1}{10}$ mm. diameter, but only for spheres which do not exceed this size. Larger ones must be treated by formulæ for pressure similar to those for a normal plane of equal circular section, with a factor of one-half for rotundity, adding a viscosity term which becomes less and less important as the size of the drop increases.

It can be shown from the experiments of Poiseuille that the linear velocity of flow of water through a fine capillary tube, where the velocity is so slow that there is no slip on the wall and no turbulent motion, may be represented by the equation,

$$v = \frac{r^2 \Delta P}{8\eta l},$$

where r is the radius of the tube, ΔP the difference of pressure at the ends of its length (l), and η the viscosity, and the same equation serves equally well for the flow of a gas. Here again Maxwell's coefficient gives results which are correct, but if we attempt to extend the application of the formula to include such results of engineering practice as those for large tubes and considerable velocities, which have been given above, we shall find that η must be increased between twenty and thirty times for a $\frac{1}{4}$-inch tube and still more for larger sizes, which agrees with the preceding demonstration of the inapplicability of the Maxwell coefficient to the conditions of the soaring aëroplane. The linear velocity of air flowing rapidly through tubes of large section is given by the equation,

$$V^{1.85} = \frac{r \Delta P}{2Hl}.$$

I have for some time recognized that Langley was wrong in neglecting viscosity, and in a lecture delivered before the Boston Scientific Society in February, 1908,[1] I demonstrated that viscosity is not only *not* negligible, but that it is most intimately involved, indeed is the very foundation of Langley's own theory, since if it were not for viscosity it would be impossible for a soaring aëroplane to virtually "take hold

[1] Reported in the Boston Transcript for February 27, 1908.

of" a body of air of many times its own extent and be held up by the inertia of the air.

In the case of an unsupported horizontal plane carried in a horizontal direction through the air there is no force developed which can produce upward motion at any speed. The case is therefore different from that of an inclined plane, which reverses its vertical motion at the critical soaring speed. The horizontal plane can have its rate of fall diminished indefinitely as the speed increases, but without the rate ever becoming zero.

If an aëroplane in calm air is standing still, its fall will be resisted by the minute amount of air friction given by the theory, calculated for the natural unit of time, the plane taking hold of a shell of air which surrounds it on every side, except to the extent that discontinuity may be produced by slip; but let the plane move along rapidly and motion is communicated successively to a large number of similar air shells, the total resistance to the fall being equal to the sum of the support offered by the individual air shells, whose number depends upon the effective distance of propagation of the viscous resistance during the time of passage of the plane.

At the speeds we have used, the gas molecules have time to move out to a distance of several feet as the plane passes, but the Langley multiple plane experiment indicates that the effective air shell is comparatively shallow. The principal part of the air support is derived from molecular collisions in the intricate, interlacing paths within a short distance from the plane. The unit of time to be employed is the time needed to transfer the motion of the plane to the *effective* air shell — a very small fraction of a second. At the beginning of motion from a state of rest, the supporting air shell is of zero depth. The depth of the shell continues to increase as relative motion is imparted to the solid and its surrounding medium, successively more and more remote layers of air being brought under the viscous control until the maximum depth possible for the given velocity and viscosity is reached. Time is required for the development of the system, as well as for its continual reproduction. The inertia of the air shell is small compared with that of the heavy aëroplane, but the energy transferred is the kinetic energy developed in the plane by gravity during the interval of time needed for its transfer to the air, which is exactly equivalent at the soaring speed. This natural time interval, or transfer time of an equivalent energy, is of course a variable quantity, becoming

shorter as the temperature rises and the molecular collisions within a given space become more numerous.[1] If the speed is doubled, the plane remains in a given region of the air only half as long, the air molecules can only move half as far, the dimensions of the supporting air shells are half as great, or there are twice as many of them as before in the same length of path. If the effective air shells were no more numerous than before there would still be twice as many individual shells threaded in a unit of time at the double velocity, and with twice as many individuals in the unit of length the air effect will be four times as great at double the velocity. The time of fall (t) of a horizontal plane through a space ($s = V_o t_o$) is therefore given by the formula,

$$t = t_o + t_1 V^2,$$

where V is the horizontal velocity, V_o is the velocity of fall for $V = 0$, t_o is the time of fall for $V = 0$, and t_1 is a constant, or nearly a constant time interval, varying only slightly with change of temperature of the air.

In a series of experiments with a horizontal plane of 30 inches transverse dimension and 4.8 inches in the line of flight, exposing a horizontal section of 1 square foot, I obtained with the Langley plane dropper at different speeds, times of fall through a space $s = 1.22$ meters, which are represented by the formula,

$$t = 0.5 + 0.00278\, V^2,$$

V being given in meters per second.

Speed of Plane.	Time of Fall.
0 meter per second	0.5 second $= 0.5 + 0.0$
6 meters per second	0.6 second $= 0.5 + 0.1$
12 meters per second	0.9 second $= 0.5 + 0.4$
24 meters per second	2.1 seconds $= 0.5 + 1.6$
48 meters per second	6.9 seconds $= 0.5 + 6.4$

Let us suppose, for example, that the effective diameter of a supporting air shell in the direction of the line of flight at the highest speed was ½ meter for this plane, or that, at least virtually, the support was transferred to a new mass of air ninety-six times per second.

[1] In the absence of viscosity the process would have no limit save that given by the boundary of the atmosphere, and the natural time interval would be greatly extended.

Then the space fallen through during the time of the first transfer was $s = \frac{1}{2}gt^2 = 0.53$ mm., the total distance fallen in 6.9 seconds being, as in the other cases, 1.22 meters.

Langley's one-fiftieth of 1 per cent. is not a bad estimate of the retardation by the air in a fall of ½ mm. from a state of rest, but at the speed which he took for his illustration, 100 feet per second, we should have, instead of a skin friction of 0.0002, a resistance due to internal friction of the air and skin friction equal to many times this quantity. At the highest speed of the preceding table, for example, we might expect a resistance from internal friction of the air and skin friction equal to $96 \times 0.0002 = 0.0192$, and it is probable that the viscosity effect is a quantity of this order, although considerable uncertainty remains as to the dimensions of the effective air shell. Zahm's experiment, allowing something for slip, favors the supposition that the effective supporting air shell may have been a little over 1 meter in length.

If we let $\Lambda =$ the number of transfers to fresh air masses per second, the natural time interval or time of transfer to which I have alluded is $1/\Lambda$. Besides varying with the speed, the quantity Λ, to which the supporting power of an aëroplane is directly proportional, varies greatly according as the plane meets fresh layers of air, or air which has already been disturbed by some antecedent member of a train or by a previous movement of the same member. If the air has previously been set in motion in such a way that it tends to slip away from the advancing aëroplane, the latter loses its grasp on the air to this extent. Such an antecedent disturbance may be either advantageous or disadvantageous. In the flapping of a bird's wing advantage is taken of the result of a previous motion by a suitable alteration of the angle of the wing plane. With a plane at a fixed angle, all previous disturbance of the air is disadvantageous. In actual aërodromics the condition of turbulence in the air will no doubt be the usual one, and plans must be laid accordingly. A large-scale turbulence of the air may be disastrous in its consequences, but intricate, interlacing vortices on a small scale ought to increase the internal friction and give a plane a better hold on the air.

The viscosity resistance cannot increase as the square of the velocity when the speed approaches that of sound, nor at low speeds where there is much slip, but the exponent 2 is about right for medium velocities, at least where there is turbulence.

While aërial friction will retard the velocity of an aërodrome at very high speeds, and will thus limit the attainable speed, skin friction is essential to the efficiency of an aërodrome, and up to a certain point the greater the skin friction the better is the grasp on the air and the larger is the sustaining power.

WESTWOOD, MASS., July, 1908.

APPARATUS AND EXPEDIENTS IN THE BACTERIOLOGICAL LABORATORY

By STEPHEN DeM. GAGE, S.B.

In the modern Public Health Laboratory the time of the scientific staff is largely occupied by routine work, and, an increase in the laboratory force being impossible, it is often a difficult problem so to arrange the work that attention may be given to the special investigations which are so necessary to keep the laboratory in touch with modern progress. The solution of this problem usually lies in a thorough systematization of the routine, and in the installation of time-saving devices and other apparatus specially adapted to the work. In many instances the infinite number of minor details of which bacteriologic technic is composed, and the opportunities for time saving a close study of those details will show, are not recognized. An illustration of this may be drawn from a recent investigation at Lawrence of the pollution of shellfish, in which tests for *B. coli* and the sewage streptococcus were required on the shell-water and intestines of from two to ten individual clams or oysters from a large number of sources. In the process of making these tests, a total of over 400 distinct manipulations were required in the analysis of each clam, exclusive of those incidental to the preparation of media, cleaning and sterilizing apparatus, and recording and reporting results. When we multiply this total by the number of samples examined, it is readily seen how a slight change in the technic, the elimination of superfluous motions, or the introduction of some time-saving device or specially designed apparatus may result in a material saving of time.

At the Philadelphia meeting of the Society of American Bacteriologists, in 1904, the writer described informally some of the methods, expedients, and special apparatus in use at the Lawrence Experiment Station of the Massachusetts State Board of Health, and recent requests for information indicate that many of these features are practically unknown elsewhere, and may be of sufficient interest to warrant their publication at this time. The various devices described have been

evolved from suggestions by members of the laboratory force, or have been copied or modified from those in use in other laboratories. Since, in many instances, the originators of the ideas are unknown to the writer, and it is impossible to give due credit to all, they are presented merely as types which have proved their usefulness at Lawrence.

Laboratory Equipment.—In equipping a laboratory, usefulness and durability should be the primary consideration, and, wherever possible, apparatus which is to receive hard usage should be made of metal, rather than of glass. Glassware, especially test tubes, should be sufficiently strong to stand rough handling. The first cost of thin tubes is less, but the loss from breakage is much greater than with heavier tubes, and the operator unconsciously wastes considerable time in the effort to prevent this breakage.

A sufficient stock of all common glassware and supplies to meet any possible emergency should be carried in stock. All common glassware should be cleaned as soon as received, and stored in a clean, dust-proof place, while sample bottles, Petri dishes, etc., should be sterilized and wrapped in paper, or placed in dust-proof boxes ready for instant use. Nothing causes so great a waste of time during a rush of work as a shortage of apparatus. About three-fourths of the cost of operating a bacteriological laboratory is expended in salaries, and a proper and plentiful equipment will pay for itself many times over in the increased efficiency of the laboratory assistants.

Method of Cleaning Apparatus.—All glassware, bottles, tubes, plates, pipettes, etc., are soaked over night or boiled for half an hour in a strongly alkaline permanganate solution, rinsed, treated with oxalic acid, and then washed five times with water. The alkaline permanganate followed by the oxalic acid is a far more satisfactory cleaning agent than is chromic acid, and the former is a waste product from the ammonia distillations in many water laboratories. The oxalic acid is used as a saturated solution to which about 2 c.c. commercial sulphuric acid per liter is added. The permanganate solution contains about 8 grams potassium permanganate and 40 grams caustic soda or potash per liter, and is diluted with ten to twenty parts of water for use. If the strong solution of permanganate is boiled thoroughly before use it is less likely to stain the hands. Both permanganate and oxalic solutions ready for use are conveniently kept in large, wide-mouthed crocks. Tubes containing solid media, and plates containing gelatin, are boiled out with water before being treated with the cleaning fluids, but only a preliminary

rinsing is necessary for tubes containing fluid media and plates containing agar. Tubes to be cleaned are placed on end in straight-sided enameled dishes, a sufficient number of tubes being used to completely fill the dish, and all operations of cleaning carried out with the dishful of tubes handled as a unit, the dish being dipped into the crocks of cleaning solutions and into a large dish of water in washing, the tubes being kept in place when the dishes are emptied by a circle of wire netting placed on top. After washing, the wire netting is removed, the dishful of tubes inverted upon a towel, the dish raised about 3 inches and a strong rubber band slipped about the block of tubes, thus holding them in place so that the dish can be removed. Tubes placed in this way dry more quickly than when placed in draining racks, the water being absorbed by the towel, from which it evaporates rapidly. When dry, the whole block of tubes may be transferred to the storage drawer before removing the rubber band. Petri dishes are handled in much the same manner, bottoms and covers being placed in separate dishes during the cleaning operations, and kept separate until dry and ready to be matched up for use. Fermentation tubes, the simple bent tubes without foot are most convenient, are packed in wire baskets holding about forty tubes, and the basket of tubes handled as a unit. A tall glass cylinder filled with permanganate solution stands upon the planting table, in which pipettes are placed as soon as they have been used, the operations of cleaning and washing the pipettes being completed in the cylinder, after which the surplus water is shaken from the pipettes and they are transferred without further drying to the metal boxes in which they are sterilized and stored.

For washing bottles it is desirable to have a bottle washer. Two of these are in use at Lawrence, one for large bottles, and one on which eight small bottles may be washed at one time. The jets on the small washer are arranged in two sets of four each, so spaced that four bottles may be picked up and placed on the washer with one hand in one motion. Both washers are connected with the city water mains by swivel joints, in order that they may be swung back against the wall when not in use, and have shut-off cocks with long handles for controlling the flow of water.

Labeling Media.—When a number of different media are used in a laboratory it is advisable to have some quick and ready means of distinguishing one from another. While the use of written labels may serve this purpose, much time will be wasted in their use, since each

basket of media must be labeled separately, and unless marked very conspicuously such labels must be examined at close range. At Lawrence written labels have been entirely dispensed with, the different media being distinguished by the use of different sized tubes and by cotton plugs of different colors.

All solid media are placed in tubes 6 inches long by about ½ inch diameter, while all fluid media are placed in tubes 5 inches long by about ⅜ inch diameter. After the medium is tubed, a solution of dye is sprayed upon the plugs with an atomizer, a distinctive color being used for each medium. For example, gelatin and nitrate solution are colored red, lactose agar and Dunham's solution are colored blue, etc., the distinction between the gelatin and the nitrate solution, and between the lactose agar and the Dunham's solution, etc., being made by the different size of the containing tubes. The dyes penetrate the cotton to such an extent that the distinctive color may be readily recognized even after the cotton plugs have been flamed. The use of jewelers' cotton of different colors has been suggested for the same purpose, but this requires that tubes of different colors be kept separate before filling with media, while by the use of the dyes all tubes are plugged with raw cotton and are available for any media for which they are suitable. For applying the dyes, the small metal atomizer used by artists to fix charcoal drawings is preferable to druggists' atomizers, being readily cleanable, only one being necessary, irrespective of the number of colors employed. Media marked in this manner are readily distinguished across the room or in the darkest corner of the incubator or storage closet, while with written labels the basket of media must be removed to the light or one must cross the room to inspect the label closely before the media can be identified.

Pipettes.—For use in a water laboratory, where a large number must be handled daily, the bulb pipettes furnished by apparatus dealers are far from satisfactory. Owing to the projecting bulb they cannot be readily drawn from the box in which they are sterilized and stored without danger of pulling out one or more upon the table or upon the floor, and when handled in bulk during cleaning and sterilizing the breakage is excessive. For a number of years straight pipettes made in the laboratory have been used at Lawrence with entire satisfaction. Two sizes are in general use, both 10 inches long, made from No. 3 tubing, one calibrated to deliver 1 c.c., and the other calibrated to deliver either 1 or 2 c.c., the latter being made with a slight lip, in order that

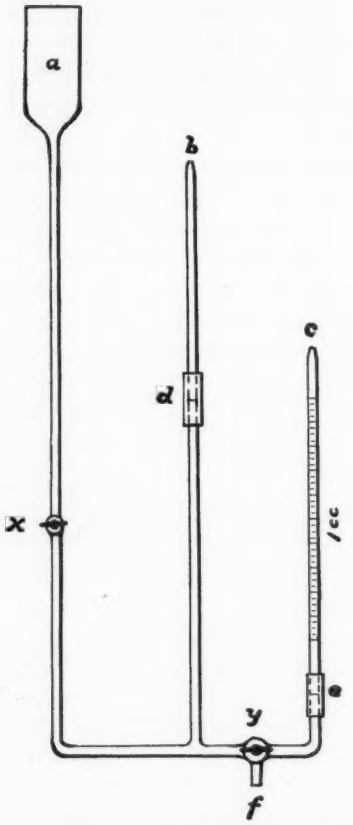


FIG. 1.—APPARATUS FOR CALIBRATING PIPETTES

the two sizes may be readily distinguished when contained in the same box. It is convenient also to have a few pipettes made from larger tubing and calibrated to deliver 10 c.c. Both large and small pipettes are calibrated in the apparatus illustrated in Figure 1, the operation being as follows: The apparatus is filled with mercury, the meniscus carefully adjusted to the lower mark in the capillary pipette *c*, and both stopcocks closed. An uncalibrated pipette *b* is inserted at the slip joint *d*, and the cock *x* opened until it is entirely filled with mercury, when cock *x* is closed and the three-way cock *y* opened, allowing the mercury to flow from *b* until it rises to the upper mark in the capillary pipette *c*,

the level to which the mercury has fallen in *b* being marked with a fine file. The mercury is then drawn from the pipette *b* and down to the lower mark in the capillary pipette by means of the three-way cock, flowing out through the waste vent *f* into a beaker, whence it is returned to the reservoir *a* as necessity requires. By means of the slip joint at *e* the capillary pipette may be removed and one of larger capacity inserted when it is desired to calibrate large pipettes. In an earlier form of calibrating apparatus, which has already been adopted into some other laboratories, the capillary pipette was omitted, the mercury being drawn from the uncalibrated pipette into a beaker placed on the scales, the volume being determined by the weight of mercury withdrawn. With the apparatus illustrated calibrations can be made much more rapidly than with the older type, and the accuracy is fully as great. If preferred, instead of marking the calibrations with a file, the pipette may be coated with paraffin and the mark made in this, the calibration being afterward etched in with hydrofluoric acid. The objection that file-marked pipettes break more easily than those which are etched appears to be theoretical rather than practical, however, and file marking is much quicker. The time consumed in making pipettes in the laboratory is small, and is more than offset by their convenience and the low rate of breakage. The average laboratory assistant can make and calibrate the 1 c.c. pipettes at the rate of two to three dozen per hour with a little practice.

Dilution Bottles.—In the analysis of sewage, milk, and many waters, dilution of the sample with sterile water is necessary before plating, the water for dilutions being usually measured out into flasks or bottles before being sterilized, and the actual volume measured after the dilution has been made. For this purpose the green glass bottles commonly used by liquor dealers, called registered flasks, are less liable to be broken, and fully as convenient as the more expensive Erlenmeyer flasks or laboratory bottles commonly used. Two sizes of these are used at Lawrence, a half-pint size containing 99 c.c. of water, and a quart size containing 499 c.c. of water. By using both 1 and 2 c.c. pipettes, and combining the bottles in various ways, a great variety of dilutions are available. The use of 2 c.c. pipettes, in this case, introduces a small error, but as the probable error of any quantitative bacteriological analysis is about 5 per cent., this small error may be neglected. The bottles are filled with a definite amount of water, plugged hard with cotton, and sterilized in the autoclave. During sterilization, a certain amount of water is lost, but if care be taken to always operate the auto-

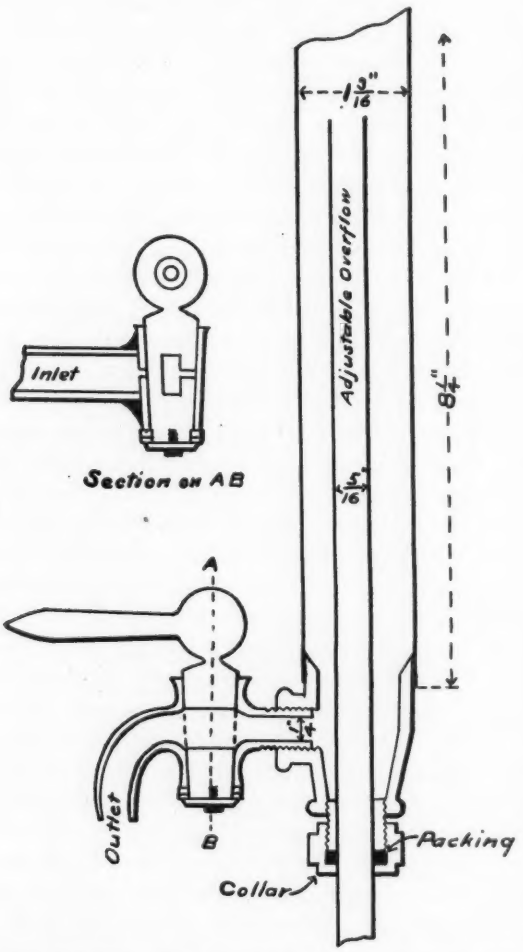


FIG. 2. — AUTOMATIC APPARATUS FOR FILLING DILUTION BOTTLES

clave in exactly the same manner, this loss will be constant and can be corrected for when filling the bottles, thus doing away with the necessity of measuring the volume in each bottle when the dilution is made.

For filling dilution bottles, the apparatus illustrated in Figure 2 will be found to effect a considerable saving of time when a large number must be filled daily. This consists of a reservoir in which the water is

measured, an overflow tube by which the volume is regulated, and a three-way cock which serves both to fill and empty the reservoir. The overflow tube passes up through a packed joint into the reservoir, and may be moved up and down while the apparatus is being calibrated to deliver the required volume of water, after which it is locked securely in position by tightening the collar through which it enters. The side arm of the three-way cock is connected directly with the city pressure by a long arm, a swivel joint permitting the apparatus to be swung back against the wall when not in use. The orifice through which the water enters the three-way cock from the city mains should be quite small, about $\frac{1}{32}$ inch for a pressure of 60 pounds, otherwise the pressure will throw the water out of the reservoir. The apparatus is made entirely of brass pipe fittings, and can be constructed by any first-class tinsmith at a cost of two to three dollars. If trouble is experienced in obtaining a proper three-way cock, one may be readily made from an ordinary lever faucet by boring a hole through the side and soldering on a side arm, this being the form shown in the illustration.

Counting Colonies of Bacteria.—It is often necessary in water or milk analyses to enumerate separately the total number of colonies on a plate and the number of each of one or more types, as, for example, the total number and the number of liquefiers on gelatin plates, or the total and red colonies on litmus-lactose agar plates. It is the custom of most bacteriologists to make such counts separately, going over the plate two or more times for the purpose. It is quite possible, however, to make two counts at the same time by carrying the total count mentally and recording the special colonies as they appear under the counting lens upon a mechanical tally or lumber counter. With a little practice, double counts made in this way are fully as accurate as are two separate counts, while the total time required for counting is reduced nearly one-half, in addition to the relief from eye fatigue which is the usual accompaniment of a large amount of routine counting.

Transportation of Samples.—Samples of water for bacterial analysis which are collected at a distance from the laboratory must be packed in ice during transportation. For this purpose shipping cases consisting of a wooden box with an inner metal compartment for the sample bottles have proved serviceable at Lawrence. The boxes are made from thoroughly dry pine lumber, which has been filled with paraffin to prevent warping, and all joints are made with screws to facilitate replacing any part which may become broken. The construction is shown in

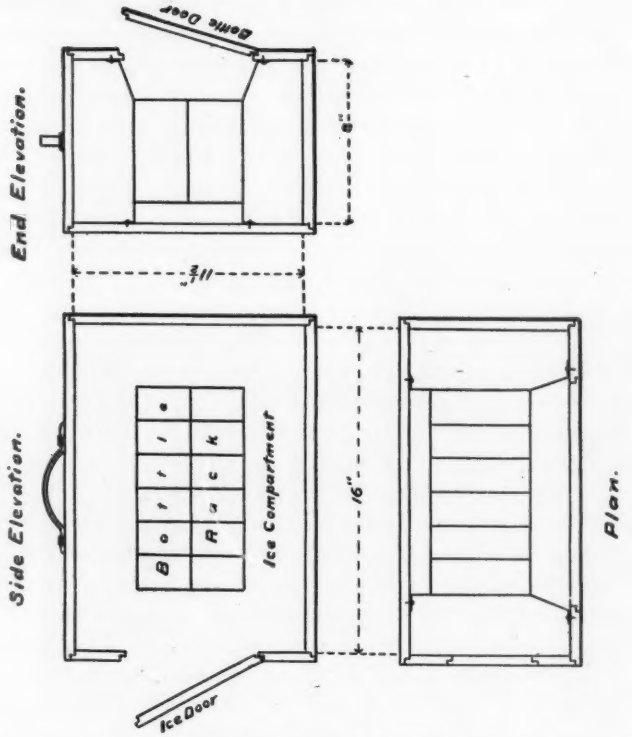


FIG. 3.—CASE USED BY MASSACHUSETTS STATE BOARD OF HEALTH FOR SHIPPING SAMPLES OF WATER FOR BACTERIAL ANALYSIS

Figure 3. Before collecting samples, the outer compartment surrounding the samples is filled with a mixture of about equal parts of sawdust and ice, broken to the size of a hen's egg. The sawdust is sent out with the cases, as it is often difficult to obtain in the field. Samples packed in this manner may be kept at a temperature of about 40° F. for twenty-four hours or more, and analyses obtained which will be sufficiently accurate for all practical purposes. For this work, 8-ounce tall Blake bottles with glass stoppers are used, it having been found by experiment that there is less change in the bacterial content of water in bottles of this size than in smaller bottles. After sterilization, the bottles are capped with paper caps held in place by rubber bands, wrapped in heavy glazed manila paper and sealed, the wrapper protecting the bottle from

breakage during transportation and from contamination by dust and dirt when stored for some time before use. When collecting samples, the paper wrapper is either removed and replaced or is merely torn away from the neck of the bottle, at the option of the collector. The bottles, wrappings, etc., are well shown in the photograph, Figure 4.

A Thermo-Regulator.—It sometimes happens that the temperature regulator for an incubator is broken, and some delay must ensue before a new one can be obtained. In such an emergency a regulator similar to the one shown in Figure 5 was tried a number of years ago, which proved so satisfactory that the one illustrated was placed permanently

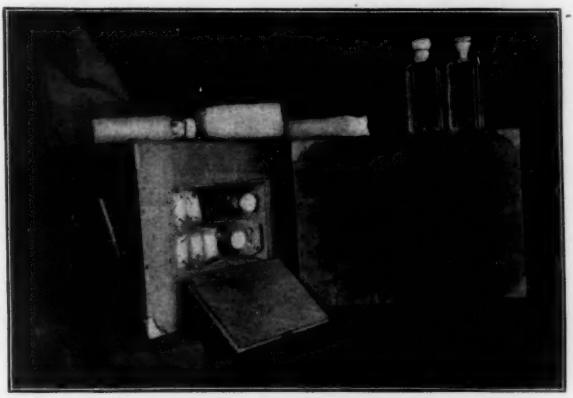


FIG. 4.—PHOTOGRAPH OF SAMPLE CASE SHOWING WRAPPED BOTTLES

on the 40° incubator. This is a modification of the well-known Dunham regulator, consisting of a large bulb filled with alcohol connected with a long U-tube filled with mercury. Passing through a T into the open end of the U-tube is a smaller tube, adjustable with reference to the height of the mercury, through which the gas passes into the burner, the flow of gas being regulated by the expansion and contraction of the alcohol acting on the mercury column. A by-pass with a small stopcock admits sufficient gas to the burner to maintain a pilot flame at such times as the flow through the adjustable tube is cut off. In the permanent apparatus illustrated, only those parts coming in contact with the mercury are of glass, the rest of the apparatus, except the flexible connection, being of brass, small gas fittings being used wherever possible.

An emergency regulator may be made up on these lines in an hour

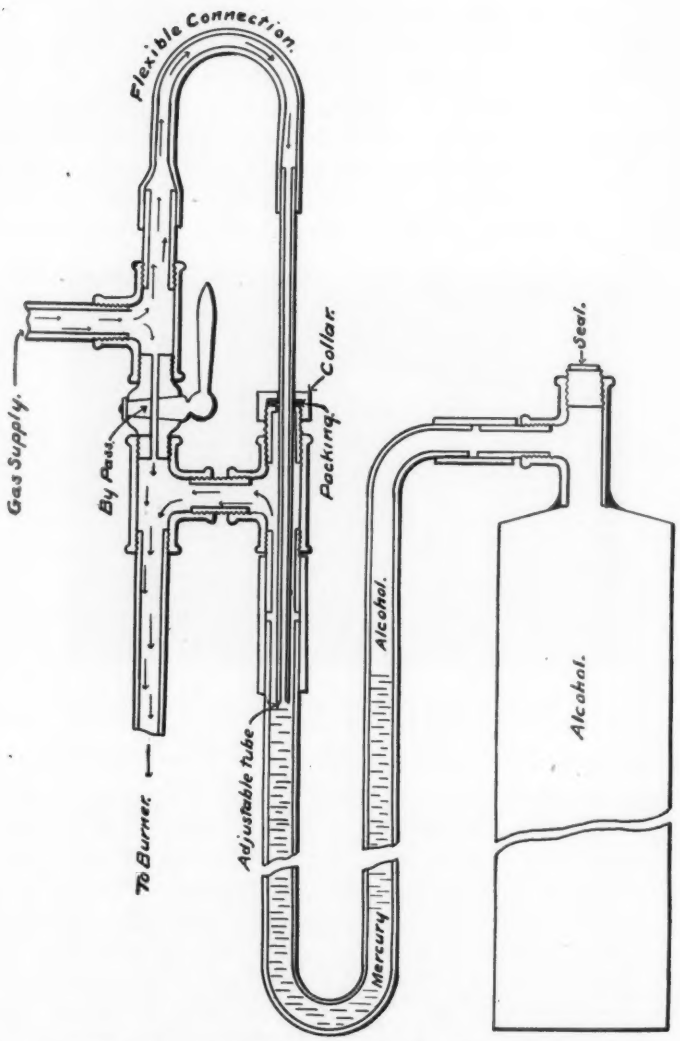


FIG. 5.—THERMO-REGULATOR USED ON 40° C. INCUBATOR AT LAWRENCE EXPERIMENT STATION

FIG. 6. — WASH BOTTLE FOR STERILE WATER

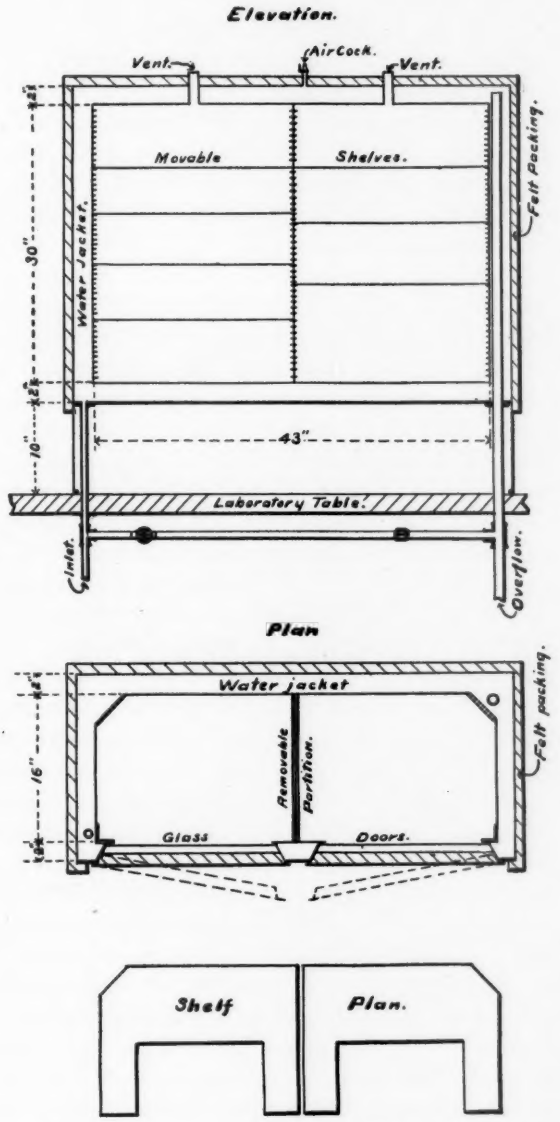


FIG. 7. — INCUBATOR FOR 20° C. WORK AT THE LAWRENCE EXPERIMENT STATION

or two, using a bottle or flask for the alcohol reservoir, a small pinchcock for the by-pass, and glass and rubber tubing for the other connections, in case brass fittings are not at hand. If brass or glass T's are not available, emergency ones may be made by cutting a small hole in the side of a piece of heavy rubber tubing and inserting a piece of glass tubing, with one end upset to form a wide lip. If the glass tubing is slightly larger than the hole in the rubber, the joint will be perfectly tight when new, and will answer for ordinary gas connections or even for water under low pressure.

A Wash Bottle for Sterile Water.—In certain procedures it is necessary to wash samples with sterile water. For this purpose the wash bottle shown in Figure 6 is easily made, and has done good service in the shellfish investigations previously mentioned. This consists of a half-gallon bottle fitted with a two-hole rubber stopper, through which pass a thistle tube plugged with cotton and a syphon of glass and rubber. The discharge end of the syphon passes through a rubber stopper in the neck of a small bottle from which the bottom has been removed, the tip being located well up inside the small bottle, where it is protected from contamination during use. A pressure pinchcock placed close to the small bottle enables the operator to regulate the flow and direct the stream of water with one hand, leaving the other hand free to hold the sample. By plugging the bottom of the small bottle with cotton and coiling the rubber tube about the large bottle, the whole apparatus may be sterilized in the autoclave without difficulty.

Twenty-degree Incubator.—In 1903 a large incubator was built for the 20° work at Lawrence which embodies some features not generally found in apparatus of this kind. The incubating chamber is surrounded by a water-jacket so designed that a constant circulation of water may be maintained, the water entering at the lower front left-hand corner, flowing completely around the incubating chamber to an overflow diagonally opposite, the flow of water being controlled by a stopcock with a graduated scale (not shown in cut) placed on the inlet pipe. A by-pass connecting the inlet with the waste pipe permits the water-jacket to be drained by opening a valve, both water valves being placed below the table on which the incubator stands, where they are easily accessible. The walls of the water-jacket are of heavy tinned copper, strongly cross-braced to prevent bulging, all joints being double-seamed and filled with solder for additional strength. The water-jacket is insulated by a thick layer of non-absorbent felt, covered by an outer casing

of galvanized iron, this outer casing being made in sections and fastened by screws, in order that the insulation may be readily removed and repairs made should occasion arise. Double doors are provided, the outer packed with felt and the inner of glass through which the contents of the incubator may be inspected without disturbing the temperature. Both inner and outer doors are fitted with piano hinges and heavy cleat catches. The outside finish is of dead black enamel, except the doors, which are of dull copper, and the trimmings, which are of lacquered brass. The incubation chamber is divided into two compartments by a perforated partition, each compartment having a capacity for about 1,000 standard size Petri dishes or thirty-six baskets of test tubes. The shelves are arranged around three sides of each compartment for convenience in getting at the contents and to allow space for tall apparatus, and are adjustable for height, being supported at one end by lugs on the partition, and on the opposite corners by cleated racks. The central partition, shelves, and shelf-supports are all removable, leaving the walls of the incubating chamber clear for cleaning or sterilizing, if necessary. The details of construction are shown in Figure 7.

A number of devices have been suggested for controlling the temperature of large incubators operated at 20° C., but these were considered either too complicated or too expensive to install and operate. Attempts were made at first to regulate the temperature of this incubator by passing the inflowing water through a coil heated by a gas burner, the flame of which was controlled by a thermo-regulator inside the incubator. This apparatus, while simple and perfect in theory, did not work well in practice, and was abandoned after about a year's trial for the present method of control. This consists of a gas burner placed directly under the incubator, connected with a Roux thermo-regulator. During hot weather a circulation of water from the city pipes is maintained sufficient to keep the temperature down within the limits at which the thermo-regulator can act, the amount of water flowing through the system being regulated by hand, and the exact temperature being controlled by the automatic regulator and gas flame. With an inspection morning and night, this method of control has proved fairly satisfactory, and a temperature of 20° C. has been maintained with a fluctuation of not over 1°. Fortunately the temperature of the city water never runs as high as 20° C., otherwise it would be necessary to pass it through an ice coil before admitting it to the incubator.

BOOK REVIEWS

Tables for Engineers and Architects[1]

This very useful set of tables contains in the revised edition, in addition to the tables given in the previous edition, the following:

A 5-place table of logarithms;

A 5-place table of logarithmic sines and tangents varying by 10 seconds from 0° to 3°, and of cosines and cotangents varying by 10 seconds from 87° to 90°;

A complete table of logarithmic trigonometric functions varying by minutes;

A table of natural trigonometric functions varying by 10 minutes;

A collection of trigonometric formulæ; and a table of decimal equivalents of inches, expressed in feet.

The old portion of the tables has been revised and enlarged to contain tables of logarithms of feet, inches, and fractions of an inch, varying by 1/32 of an inch from 0 to 50 feet, and by 1/16 of an inch from 50 to 100 feet; and parallel with these, the squares of these distances. This table is very useful in mensuration, and also particularly in the solution of triangles for figuring the data required for structural detail drawings in which it is necessary to get the precise lengths of diagonal members. The table of squares of distances, as well as the table of logarithms, is frequently very useful, and in some cases the logarithm and the square are both useful for the solution of the problem.

The book also contains the angles and logarithmic functions corresponding to different so-called bevels, the bevel being the height of a right-angled triangle which has a base of 12 inches. This table, also, is of great usefulness in structural computations; for instance, for a right-angled triangle, if one side is given and the slope of the hypothenuse, the other side may be quickly found.

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[1] Smoley's Tables: Parallel Tables of Logarithms and Squares for Engineers, Architects, and Students. By Constantine Smoley, C.E. 5th edition revised. New York: The Engineering News Publishing Co.

The previous edition contained the table of logarithms and squares only up to 50 feet. In the present edition, as already stated, this table has been continued to 100 feet. In this edition, also, there has been added a multiplication table for rivet spacing which is very convenient in the designing of rivet work.

The book will be found very useful by structural designers.

G. F. S.

Graphical Determination of Earth Slopes, Retaining Walls, and Dams [1]

Graphical methods are found valuable for many purposes, and this treatise sets forth their application to earth pressures and to retaining walls, structures designed to resist these pressures, but also includes dams, which can logically be treated in the same connection. The book is intended for the use of students rather than engineers in practice, and is purposely made less complete in the elaborate discussion of theories than would otherwise be the case.

The author has found, as might be expected, that the results obtained by graphical methods compare satisfactorily with those analytically obtained. In fact, earth pressures would appear a very suitable field for graphical treatment, since our knowledge of the data involved does not justify great precision in results. It is interesting to note that for the analytical theories considered, recourse is had to Rankine, that wonderful mathematician who has ably treated so many engineering subjects that it is never out of place to consult his books, however ancient they may seem.

The graphical methods used are largely those of Culmann, Rebhann, Weyrauch, and Blanc, and the book is thus mainly a compilation, or rather an adaptation, than it is a purely original treatise, although we must except the graphical determination of earth slopes of uniform stability.

The author apparently has had the opportunity to use more or less of this treatise with his students at Manhattan College, an advantage which tends to secure clearness of presentation. Although prepared

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[1] Graphical Determination of Earth Slopes, Retaining Walls, and Dams. By Charles Prelini. New York: D. Van Nostrand Co., 1908. 129 + v pp., 75 il., 8vo.

primarily for students of engineering, practicing engineers who have not specially pursued this subject elsewhere may readily find this book interesting and instructive.

Chapter I deals with the stability of earth slopes.

Chapter II with retaining walls by graphical methods.

Chapter III the same by analytical methods.

Chapter IV takes up the design of retaining walls.

Chapter V adds dams or walls subjected to water pressure.

In its typographical and mechanical make-up the book is satisfactory.

Highway Bridges [1]

In this rather elaborate work the author attempts to cover a wide field, treating not only of the computation of stresses on simple trusses, but carrying this as far as the treatment of the arch without hinges; also covering the design of highway bridges of wood, steel, stone, concrete, and reënforced concrete, as well as of piers, abutments, culverts, etc.

Part I treats of the stresses in steel bridges, both for highways and railways, from the simple beam to rather complicated but usual truss forms. Stresses in pins and in other minor parts, in portals and lateral systems, are taken up, and a large number of problems given to illustrate. Some of these last might as well have been omitted, as, for instance, the determination of dead stresses graphically, which method probably nobody familiar with analytical methods would ever use.

Part II treats of the design of highway bridges of all kinds and materials, giving specifications, detail drawings, and tables of weights, costs, etc.

We cannot but wish that the author had confined himself to a smaller field, and had treated some parts more fully. The book is somewhat lacking in balance, some parts being rather sketchy, while others are treated in too much detail. Nevertheless, it contains much valuable information, and will no doubt be useful to many engineers who have mainly to do with highway bridges. It is well printed and illustrated, and bears the marks of careful preparation. G. F. S.

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[1] The Design of Highway Bridges and the Calculation of the Stresses in Bridge Trusses. By Milo S. Ketchum. New York: Engineering News Publishing Co., 1908.

HYDRAULICS [1]

THIS work is one which every teacher of hydraulics will wish to have upon his shelves as a reference book, but as a text-book for use in American engineering schools it will probably not have a very extended use.

The first half, that dealing with hydraulics proper, takes up all of the topics usually discussed in such a work, but more than the usual amount of space is devoted to the physical properties of water and the motion of fluids. The equations for the latter are developed in a manner which is probably beyond the student of ordinary mathematical ability. The same may perhaps be said of certain other portions of the work, and for this reason it will not appeal, as it should, to many students of the subject in this country.

In the first chapter are discussed the physical properties of water, including cohesion, adhesion, capillarity, surface tension, and viscosity.

Chapter II, hydrostatics, takes up the usual propositions of this topic, as well as the equilibrium and oscillation of floating bodies.

In Chapter III the motion of water is considered, including vortex motion.

Then follow in order the flow through orifices, mouthpieces, and over weirs; fluid friction, the resistance and propulsion of ships; flow in pipes, including branches, and water hammer.

Uniform and non-uniform flow in open channels and stream gagings are covered in Chapter IX, and Chapter X closes the first portion with a discussion of the impulse of jets, pressures on vanes, etc.

The foregoing discussions are both interesting and satisfactory, but there is some unevenness of treatment. Weirs, for example, are allotted their due proportion of space, but there is less originality of method than is shown in many places.

Stream gagings, on the contrary, are cut short with a bare dozen pages, whereas this subject deserves much more attention in a work so comprehensive.

Chapters XI–XIX cover the applications of hydraulic principles to machinery. A brief discussion of the older forms of water wheels introduces the study of the modern forms of turbines. The American type of wheel receives rather brief notice, but, on the whole, present

[1] Hydraulics and Its Applications. By A. H. Gibson. New York: D. Van Nostrand Co.

practice is well set forth. The discussion of the theory of turbines is based upon the relations of the moment of momentum.

Losses of energy in the wheels are considered at some length, and the effects of standpipe and fly-wheel regulation are touched upon, though regulation, on the whole, receives too little attention.

Pumps, both reciprocating and centrifugal, are considered at length, and the latter are illustrated by the latest types.

The ram, air lift pump, and hydraulic air compression are considered in a short chapter, number XVII; number XVIII treats of meters and hydraulic power transmission; while the concluding chapter deals with jacks, cranes, presses, etc.

Four brief tables comprise the appendix.

The applications are well chosen and, if not described in sufficient detail for the practicing engineer, the students' needs are fully met, and more matter could probably not be introduced with advantage for teaching purposes.

The book contains over 700 pages, and is too heavy to be convenient. The type is large and clear, and the diagrams, of which there are many, are good, in striking contrast to those in another recent English work. The book is an excellent one and should do much to put the teaching of hydraulics upon a higher plane, from the theoretical side, making up in this way what it may lack as a handbook for the practicing engineer.

W. E. M.

Water-Power Engineering[1]

Into this bulky volume of nearly eight hundred pages, Professor Mead has gathered a large amount of information relating to the subject of water power. There has hitherto been no lack of literature bearing upon the many questions involved in the design of a modern water power plant—stream flow and storage, controlling works and power houses, turbines and governing devices—but this matter is widely scattered through technical magazines, professional reports, and engineering society publications. In gathering this information together and presenting its substance in a single volume, the author has rendered a distinct service to the engineering profession.

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[1] Water-Power Engineering. By Daniel W. Mead. New York: McGraw Publishing Co. Price, $6.00.

Beginning in Chapter I with a brief historical review of the subject, in the next four chapters are discussed the more general questions of energy and water power, together with so much of hydraulic theory as relates to the flow of water in penstocks, flumes, and over weirs. The backwater curve also receives attention at this point. Chapters VI–XI deal with rainfall, run-off, and the measurement of stream flow.

Then follow five chapters on water wheels, their theory, construction, testing, and such considerations as influence the selection of a turbine for particular duties.

Chapter XVII takes up the load curve and its influence upon the design of a power plant.

Speed regulation and governors are fully discussed in the two following chapters and an appendix.

The arrangement and setting of turbines, power house design, head works and dams, including appendages to the same, together with numerous examples from recent constructions, are discussed in Chapters XX–XXV. Chapter XXVI deals with pondage and storage, number XXVII with the cost, value, and sale of power; and in the concluding chapter is given a brief outline of the proper scope for a report upon a water power project.

In the eight appendixes are given more detailed discussions of some of the points presented earlier in the work and numerous tables of the results of wheel tests, as well as stream flow data.

The book is presumably written for the use of advanced students in engineering courses, and it will serve admirably to place before such students the complexity and interrelation of the problems which enter into power plant design. Nevertheless, practice rather than theory is ever uppermost in the book, which throughout bears evidence of the author's familiarity with the best practice of the day and a desire to present to his students the essentials only. Graphical methods are extensively introduced throughout the book, notably in considering stream flow, storage, and turbine performance; several of these diagrams will doubtless be quite new to the profession.

It is to this feature of the book that it owes its strongest claims to originality. If some of the topics are discussed rather briefly, their broad scope may be sufficient justification, and the reader who wishes more detail will find at the end of nearly every chapter a most valuable list of references to the literature of the subject discussed therein.

One misses in a work so comprehensive anything more than a passing

reference to the question of water rights and damages for diversion, etc. The arrangement of the subject-matter as a whole would seem to be susceptible of some improvement, following perhaps a more natural order, as indicated in Chapter XXVIII.

The book is very fully and, on the whole, well illustrated. The indexing is good, the paper and press work satisfactory. In such a large work some errors are to be expected in the first edition; but there are occasional evidences of hurried proofreading, as, for instance, in Table LIV, page 661, where the costs of fuel per kilowatt hour are given as fractions of dollars instead of cents. The same error occurs in other columns.

The work is a distinct contribution to the literature of the subject, and will be read with interest and profit by any one engaged in the important field of water-power engineering. W. E. M.

Design of Chemical Laboratories[1]

This contains much of the material found in the early chapters of books on quantitative analysis, together with the results of the author's reading and experience; a useful feature is the designation of sources of supply.

Cement concrete—as might be expected—has even found its way into the laboratory, directions being given for the preparation of foundations for balances and floors for hoods; the reviewer thinks the imbedding of pipes and joints in concrete of doubtful expediency, twenty-five years' experience having shown the value of being able to get at every inch of piping with the tongs. Regarding foundations for balances, unless there be heavy machinery in operation in the building, there is no need of brick or concrete piers; unless the building be of wood, wooden shelves can be solidly fastened to the brick walls. One searches in vain for hardened filters, and for the materials out of which laboratory desk tops and shelves are made; nor is any mention made of the use of sand or "soda water" in extinguishing laboratory fires or the employment of chloride of calcium or sulphuric acid in balance cases when weighing hygroscopic substances.

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[1] The Design and Equipment of Small Chemical Laboratories. By Richard K. Meade. Chicago: Chemical Engineering Publishing Co., 1908. 138 pp., 8vo.

It should be noted that the *agate mortar does contaminate the sample,* as Hempel has shown, and also that red rubber tubing is not as durable as the gray or zinc-filled rubber. The necessity of having the weights in constant use adjusted at least annually, and of even checking government certified apparatus, should be emphasized, as the writer has known of three cases in which this certification of apparatus was incorrectly done.

The author modestly hints that the work is intended for the young chemist, but it is a book from which even the old ones can learn something, and will be extremely useful to all those having to do with laboratories, whether chemical, physical, or biological. A. H. GILL.

THE VEGETABLE SOURCES OF DRUGS[1]

THE book is divided into two parts: Botany and Pharmacognosy.

The botanical part contains, first, a chapter giving in brief outline an account of the classification of the vegetable kingdom. Then follows a chapter on the anatomy of the higher plants, each organ being taken up separately, and this is followed by one on the histology of plants. Then comes a more detailed classification of the Angiosperms which yield vegetable drugs; after which is given a list of the medical plants found in cultivation.

These chapters dealing with so large a subject in so small a space necessarily treat the different parts briefly. This brevity of treatment is noticeable in the definitions, which are somewhat inadequate, especially the definitions of the words "morphology" and "ecology"; the word "habitat" is used incorrectly in place of "locality" or "geographical distribution"; and we note a casual reference to the hypothesis of the inheritance of acquired characteristics which would lead the student to assume that it was an accepted theory. It seems a pity that a more adequate classification has not been given, especially in the chapter on Angiosperms.

In the first chapter each group of plants is illustrated by certain well-known examples, and special stress is laid upon their different methods of reproduction. On the whole, the ground is fairly well covered. In

[1] A text-book of botany and pharmacognosy, by Henry Kraemer. Edition 3. Philadelphia: Lippincott, 1908.

some places a little fuller treatment would have been desirable, as, for example, it is rather a shock to find the yeasts placed without any qualification among the Ascomycetes, and if the division of the Basidiomycetes had been clearly shown it would make plainer the relationship of the mushrooms to the smuts and rusts.

In the chapter on the Angiosperms we note that the hemp, the fig, and the mulberry are placed together in one family, Moraceæ, without any suggestion that there is good authority for separating these types into three separate families. It is to be feared that the student studying this chapter will not have a very clear idea as to why various plants are placed in separate families and orders, as there is scarcely a hint of the characters by which these groups are separated. The definition of the poppy family is characteristic, "These are herbs with a milky or colored latex," which would apply equally well to the milkweeds.

Following these definitions, under each order, there is a more valuable account of the useful plants, with brief mention of the products obtained from them. These contain much interesting information. One small point that stuck the reviewer is that Chinese rice paper is not made from rice at all, but from the pith of a plant of the Ginseng family.

The second part of this work is probably more useful. It is divided into two chapters; the first on crude drugs, the second on the powdered vegetable drugs and foods.

The crude drugs are classified as seeds, roots, parts of roots and stems, flowers, fruits, leaves and herbs, exudations, juices, and other plant products.

Both chapters are intended to be used for the identification of drugs, and are supplied with artificial, or analytical, keys on the principle of works in systematic botany. The amount of detail in regard to each drug varies somewhat, but in general the name of the drug is followed by a statement of the name of the species and the organ from which it is derived. This is followed by a brief account of the geographical distribution of the species and the chief source of the commercial supplies.

Then follows a detailed description of the part used as the crude drug; next, a paragraph on its chemical constituents; third, a paragraph on the adulterants commonly used; and finally, a paragraph on allied drugs or plants.

The powdered drugs are classified into five groups by their color, greenish, yellowish, brownish, reddish, and whitish. These, in turn, are subdivided by various characteristics too numerous to mention. This

part of the work is well illustrated by figures, mostly drawn by the author, which will be a great help in identification. R. P. B.

Electrical Illuminating Engineering[1]

The recent developments in electric lamps of different types, together with the increasing prominence given to the subject of illuminating engineering, have created a demand for literature which gives a description of the modern electrical illuminants and which outlines the theory used and the methods of calculation employed in the design of a lighting system. The book in hand, prepared from notes used by the author in connection with his classes in illuminating engineering at Armour Institute, covers a very broad field in comparatively few pages, and as a result many points of considerable importance are either inadequately treated or entirely omitted. To be of use as a text in schools, the book should be supplemented to a large extent with lectures, as suggested in the preface. While some books now available on the subject of illuminating engineering may be criticised on account of the fact that they emphasize the particular product of some manufacturing company to too great an extent, this text is perhaps too impartial, and where several devices for accomplishing the same object are described there is little to aid one in deciding which is the most practical for any particular service.

The subject is introduced by brief chapters on light and color and on the units recommended for use in connection with illuminating engineering by the American Institute of Electrical Engineers. The next section deals with photometry and photometers, and is useful in that it brings together concise descriptions of the more recent types of photometers and illuminometers. This section would be greatly increased in its value to the reader if the practical application of the different types were discussed to a greater extent, and if some idea of the relative sensitiveness and accuracy of the different devices were given. The standards of illuminating power are treated from a historical standpoint, but particular attention is paid to the units now adapted by the various

[1] Electrical Illuminating Engineering. By William E. Barrows. New York: McGraw. 212 pp., il. Price, $2.00.

governments or national societies, and the valuable table of comparison of these units is included.

Electrical illuminants are considered under the heads of incandescent lamps, arc lamps, flaming-arc lamps, and vapor lamps. Owing to the limited amount of space devoted to these subjects there is very little descriptive matter included. The practical application of the different types of lamps is lacking. Several of the metallic filament lamps in either the experimental or commercial stage are mentioned, but there is little to aid one in determining which are or which may be employed to any great extent. Shades and reflectors are given some consideration, and the distribution curves of several of the better known types of reflectors are included.

The final chapter is devoted to the subject of illumination calculations. No new material is included in this chapter, but an attempt is made to present only such matter as will be of direct aid in calculating the illumination at a given point with the lighting sources known, or for determining the value of the light sources and their distribution when the illumination at any point is decided upon. Considerable attention is paid to the question of the arrangement of lamps for producing uniform illumination. The application of some of the formulas to specific forms of lighting could be profitably extended, and some discussion of the light reflected from the side walls and ceilings in certain installations might well be included.

There is little in the treatment of the subject that is original, but the book as a whole is valuable in that it brings together a great deal of the information desired by those interested in illuminating engineering and electric lamps. In order to apply this information intelligently in practical illumination problems, much more information than is included in the text is necessary. GEORGE C. SHAAD.

PUBLICATIONS[1]

Chemistry and Chemical Engineering

Henry Fay. — A Microscopic Investigation of Broken Steel Rails: Manganese Sulphide a Source of Danger. *Proceedings of American Society for Testing Materials*, 1908. il.

William Guertler. — Folgerungen für die Technik aus dem heutigen Stande unserer Erkenntnis des elektrischen Leitungswiderstandes der Metallegierungen. *Metallurgie*, Vol. 5, Heft 10. 5 p. 8vo.*

William Guertler. — Über die Verwendung von Rückstandsanalysen zur Festellung der Formeln von Metallverbindungen. *Metallurgie*, Vol. 5, Heft 6. 3 p. 8vo.*

William Guertler. — Bemerkungen zu dem Gesetz von Matthiessen, betr. den Temperaturkoeffizienten der elektrischen Leitfähigkeit der Metallegierungen. I. *Physikalische Zeitschrift*, Vol. 9, No. 1, pp. 29–36. 4 il. 4to.*

William Guertler. — Über die elektrische Leitfähigkeit der Legierungen und ihren Temperaturkoeffizienten. *Physikalische Zeitschrift*, Vol. 9, No. 12, pp. 404–405. 4to.*

William Guertler. — Stand der Forschung über die elektrische Leitfähigkeit der kristallisierten Metallegierungen. *Jahrbuch der Radioaktivität und Elektronik*, Bd. 5, Heft 1, pp. 17–81. 26 il. 8vo.*

William T. Hall and *George Defren.* — Text-Book of Physiological Chemistry in Thirty Lectures, translated from the German of Emil Abderhalden. New York: Wiley. 1908. 13 + 722 p. 8vo.*

F. J. Moore and *R. D. Gale.* — The Colored Salts of Schiff's Bases. — A Contribution to Our Knowledge of Color as Related to Chemical Constitution. *Technology Quarterly*, Vol. 21, No. 2, pp. 200–211. June, 1908. *Journal American Chemical Society*, Vol. 30, No. 3. March, 1908.*

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[1] In order that the extent of productive work carried on at the Institute may be better known, it is designed to publish a list of the publications of officers of the Institute, together with abstracts when possible. In this list the publications are arranged alphabetically by departments and then alphabetically by authors.

The asterisk after the title indicates that a copy of the publication has been placed in the library of the Institute.

F. J. Moore and *R. G. Woodbridge, Jr.* — The Colored Salts of Schiff's Bases, II — The Hydrochlorides of Bases Formed by Condensing *p*-Aminodiphenylamine with Aromatic Aldehydes. *Journal of American Chemical Society*, Vol. 30, No. 6, pp. 1001–1003. June, 1908.*

Arthur A. Noyes. — A Talk on Teaching. (Printed, not published.) 16 p.*

Arthur A. Noyes. — Address to New Students at the Massachusetts Institute of Technology. (Printed, not published.) 10 p.*

Ellen H. Richards. — Farm Home, a Centre of Social Progress. *Encyclopedia of American Agriculture*, Vol. 3.

Ellen H. Richards, E. M. Wade, R. N. Gilbert, C. E. Hanson, and *J. M. Talbot.* — Methods of Testing the Efficiency of Ventilation. *Technology Quarterly*, Vol. 21, No. 3. September, 1908.

Ellen H. Richards. — Cost of Cleanness. Fourth in the "Cost" Series. New York: Wiley. 1908. 104 p.

Ellen H. Richards. — Laboratory Notes on Industrial Water Analysis. New York: Wiley.

Ellen H. Richards. — Household Science in Elementary and Secondary Schools. *Proceedings of National Education Association*, June 29–July 3, 1908. Cleveland, Ohio.

H. P. Talbot. — Some Recent Investigations in the Chemical Department. *Technology Review*, Vol. 10, No. 4. 13 p.*

W. H. Walker. — The Relation of Chemistry to Street Railway Work. *Street Railway Bulletin*, Vol. 7, p. 134. 1908.

W. H. Walker. — Standard Methods of Analysis for Materials Used in Chrome-Tanning. *Journal American Leather Chemical Association*, Vol. 3, p. 267. 1908.

Civil Engineering

C. B. Breed and *George L. Hosmer.* — The Principles and Practice of Surveying. Vol. 2, Higher. New York. 1908. 432 p. 164 il. 8vo.

George E. Russell. — Notes on Hydraulics. Revised edition. Boston, September, 1908. 90 p.

The notes constitute the text for all students studying hydraulics at the Institute, save those of Course I, whose longer course has made it seem better that they should use a text and reference book. The notes are lithographed and form the nucleus of a larger and more comprehensive printed volume, which the writer hopes to publish in the near future.

Electrical Engineering

Dugald C. Jackson. — An Important Committee on Engineering Education. *Technology Review*, Vol. 10, pp. 276–280. July, 1908.

George C. Shaad. — Review of Barr's Direct-Current Electrical Engineering. *Science*, November 25, 1908.

Geology

Reginald A. Daly. — The Mechanics of Igneous Intrusion — Third Paper. *American Journal of Science*, Vol. 26, pp. 17–50. 8vo. July, 1908.

Reginald A. Daly. — The Origin of Augite, Andesite, and of Related Ultra-Basic Rocks. *Journal of Geology*, Vol. 16, pp. 401–421. Chicago, August, 1908.

H. W. Shimer. — Dwarf Faunas. *American Naturalist*, Vol. 42, pp. 472–490. July, 1908.*

The first part of the article discusses the chief causes of the dwarfing of invertebrate water-living faunas, using recent examples as illustrations; the second part considers some fossil examples with their probable causes. The chief agency is shown to be an abnormal habitat A species, for generations used to an environment of sea water with a certain unvarying density, temperature, clearness, and depth, would become so accustomed to that state of affairs that a change in one or more of the factors would affect it unfavorably.

The chief causes of dwarfing are suggested as being: (1) a change in the normal chemical content of the water; (2) the presence of mechanical impurities in the water; (3) a floating habitat; (4) variations in temperature; (5) extremes in depth of water.

H. W. Shimer. — The Pennsylvania-German as Geologist and Paleontologist. *The Pennsylvania-German*, Vol. 9, pp. 411–414. September, 1908.

The first part briefly discusses the character of the Pennsylvania-German colonists and the environment amid which they developed in this country, with the resultant type so well known from New Jersey and New York to Illinois. The second part gives a very brief biography of some of the geologists and paleontologists derived from this stock.

Mathematics

E. B. Wilson. — The Equilibrium of a Heavy Homogeneous Chain in a Uniformly Rotating Plane. *Annals of Mathematics*, Second Series, Vol. 9, No. 3, pp. 99–114. April, 1908.*

The exact solution of the problem of the figure of equilibrium of a heavy homogeneous chain in a uniformly rotating plane is apparently not to be obtained in finite form in terms of the known functions of mathematics. As the problem is one of interest, an approximate solution, therefore, seems worth while. It is this that is given in the above paper. The chief fact of physical interest is that for a given chain endowed with a given angular velocity there are a finite number of distinct positions of equilibrium which differ in the number of loops and nodes which the chain may have. There are also points of mathematical interest in connection with the approximations introduced in the solution.

E. B. Wilson. — Logic and the Continuum. *Bulletin of the American Mathematical Society*. Second Series, Vol. 14, No. 9, pp. 432–443. June, 1908.*

The article on logic and the continuum contains a critical discussion of some fundamental principles of mathematical logic which have been developed by E. V. Huntington and others, and which appear not to have acquired their merited place in discussions of the subject. These matters are then applied to the treatment of the continuum with especial reference to Zermelo's alleged proof of the possibility of well-ordering the continuum. The principal conclusion is that Zermelo bases his proof on an axiom which is more transcendent than the theorem he wishes to prove.

E. B. Wilson. — On the Principle of Relativity. *Philosophical Magazine*, pp. 419–422. September, 1908.*

The short note on the principle of relativity is in reference to a new principle of relativity for electrodynamics recently propounded by Bucherer. From a cursory examination of Bucherer's chief formula, it appears that neither his principle nor any one like it is likely to meet with favor as the ultimate foundation of electromagnetism. It may be added that we understand that he has now abandoned his principle and adopted the Lorentz-Einstein hypothesis.

Mining Engineering and Metallurgy

H. O. Hofman. — Recent Improvements in Lead Smelting. *Mineral Industry*, Vol. 16, pp. 657–693. 1907.

H. O. Hofman. — Review of A. G. Bett's Lead Refining by Electrolysis. *American Chemical Journal*, Vol. 40, p. 493. 1908.

R. H. Richards and *C. E. Locke.* — Progress in Gold Milling in 1907. *Mineral Industry*, Vol. 16, pp. 553–566. il. 8vo. 1908.

R. H. Richards and *C. E. Locke.* — Progress in Ore Dressing and Coal Washing in 1907. *Mineral Industry*, Vol. 16, pp. 960–1014. il. 8vo. 1908.

Modern Languages

John Bigelow, Jr. — Review of Trevelyan's "The American Revolution." *American Historical Review*, Vol. 13, pp. 874–875. New York, July, 1908.

John Bigelow, Jr. — The Saber and the Cavalry. Fort Leavenworth, Kansas. *Journal of United States Cavalry Association*, Vol. 19. 7 p. April, 1908.

Naval Architecture

W. Hovgaard. — A Proposed New Type of Conning-Tower for Large Battleships. *Jane's "Fighting Ships,"* for 1908, pp. 419–424. il. London.*

This is an account of recent war experiences and firing experiments, showing necessity of improvements in conning-towers, with a critical description of existing conning-towers, pointing out existing defects, and an exposition of the general principles governing the design, followed by a description of proposed location and construction of conning-towers.

W. Hovgaard. — An Analysis of the Resistance of Ships (a paper read before Institution of Naval Architects, London). *Transactions Institution of Naval Architects*, London, Vol. 50, pp. 205–222. il. April 10, 1908.

This contains general form of the mathematical expression for wave-making resistance and some remarks respecting the formation of ship waves. There is also a discussion of the form of three terms of the expression for wave-making resistance, namely, the speed term, the term involving the principal dimensions, and the term involving the fineness.

This discussion is based on an analysis of the published curves of resistance, notably those of serial experiments made by the older and younger Froude in England, by Colonel Rota in Italy, and by Naval Constructor Taylor in the United States.

In the appendix is given an explanation of the method of focal diagrams used in the analysis of the curves, together with more detailed description of the analysis.

The paper is accompanied by several plates, which show curves of resistance, focal diagrams, etc., and a table giving a summary of results.

Physics

Daniel F. Comstock. — The Indestructibility of Matter and the Absence of Exact Relations among the Atomic Weights. *Journal American Chemical Society*, Vol. 30, pp. 683–688. May, 1908.

Louis Derr. — Photography for Students of Physics and Chemistry. New York: Macmillan. 1906.

R. A. Millikan and *John Mills.* — Electricity, Sound and Light. Boston: Ginn & Co. 1908. 8vo.

Institute Publications

Massachusetts Institute of Technology. — Bulletin, Vol. 43, No. 4, Programme. Edited by Dana P. Bartlett. Boston, June, 1908. 381 p.*

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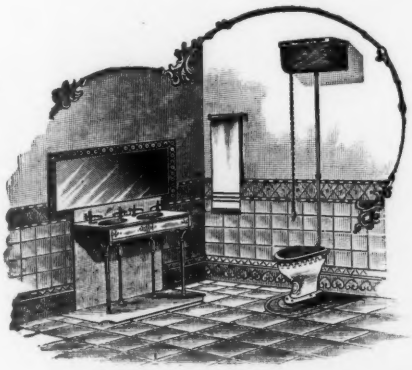

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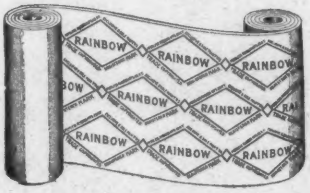

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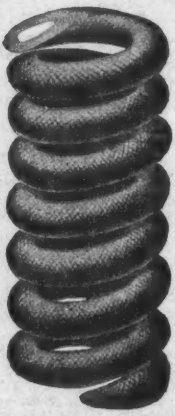

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